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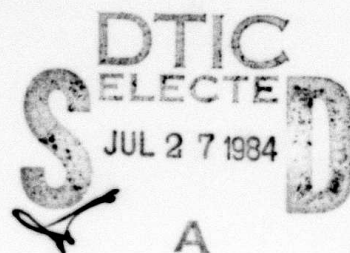
*Preliminary Reports, Memoranda  
and Technical Notes of the  
Materials Research Council  
Summer Conference*

*La Jolla, California*

July 1983

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**TITLE****PAGE**

10. Multilayer Films: Syntheses, Diagnostics, and Control, D. U. Gubser..... 462
11. The Peculiar Challenge of Chemical Processes to Advanced Control Systems, Rutherford Aris..... 468
12. Analytical Controls and Artificial Intelligence Experiences with Materials Processing Analogs R. L. Currie..... 472



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PRELIMINARY REPORTS, MEMORANDA AND TECHNICAL NOTES  
of the  
MATERIALS RESEARCH COUNCIL SUMMER CONFERENCE  
La Jolla, California  
July 1983

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## TABLE OF CONTENTS

- I. Foreword
- II. Steering Committee
- III. Participants
- VI. Preliminary Reports, Memoranda and Technical Notes

The following papers fall into two categories; (1) papers in a state ready for publication, and (2) reports and memoranda for limited distribution representing work in progress. The former category is available for general distribution and in some cases are in the process of publication in the appropriate technical journals. The limited distribution reports and memoranda represent initial ideas, problem suggestions, position papers, and status reports and are aimed primarily to stimulate discussion with the Council. However, they are available subject to the author's release by request to the Project Director.

<u>TITLE</u>	<u>PAGE</u>
Factors Governing Yield of GaAs Integrated Circuits T. C. McGill, D. K. Ferry and H. Ehrenreich.....	1
Three Dimensional Integrated Circuits D. K. Ferry, T. C. McGill, and H. Ehrenreich.....	16
Monolayer and Multilayer Thin Film Materials M. S. Wrighton.....	26
Line Defects in Langmuir-Blodgett Films J. P. Hirth.....	39
Towards Perfect Optical Coatings A. Macleod, C. M. Stickley and E. Cross.....	47
Uncooled IR Sensors L. E. Cross and C. M. Stickley.....	60
Workshop on Microstructure and Toughness; S. Fishman, J. P. Hirth, L. A. Jacobson and J. C. Williams.....	74
1. The Relations Among Ductile Fracture Topography, Ductility and Toughness, Anthony W. Thompson.....	94

<u>TITLE</u>	<u>PAGE</u>
2. Cleavage Fracture of Steel in the Ductile-Brittle Transition Region, A. R. Rosenfield.....	96
3. Fracture Toughness of Al-Li Alloys, E. A. Starke.....	97
4. Toughness in Al Alloys, E. A. Starke.....	100
5. Micro-Tough Plastic Instability and Fracture, J. P. Hirth.....	102
6. A Note on Microstructural Design for Strength and Toughness, D. C. Drucker.....	106
7. Microcrack Formation in Iron by Cracking of Grain-Boundary Carbides: A Statistical Treatment, Morris Cohen.....	111
8. Fracture Toughening of Steel by Deformation-Induced Martensitic Transformation, Morris Cohen.	113
9. Some Uses of Controlled Porosity to Improve Crack Propagation Behavior of Brittle Materials, E. E. Hucke.....	116
10. Elastic Size Effect in Microstructural Design, E. E. Hucke.....	118
11. Some Effects of Phase Transformations on Toughening, A. G. Evans.....	120
12. Use of Long Wavelength Neutrons for Evaluation of Voids in Stressed Solids, B. B. Rath.....	121
13. On Size Effects in Void Nucleation, A. G. Evans, J. W. Hutchinson and B. Budiansky...	123
14. Role of Microstructure in Influencing Fatigue Crack Propagation, R. O. Ritchie.....	128
15. Ductile Crack Extension, J. C. Williams.....	130
16. Void Growth or Void Nucleation Controlled Ductile Fracture, John W. Hutchinson.....	133
17. Micromechanics of Cleavage and the Ductile-Brittle Transition, John W. Hutchinson.....	136
Workshop on Space Materials, G. H. Vineyard and H. Ehrenreich.....	140

<u>TITLE</u>	<u>PAGE</u>
Electrochemical Energy Sources M. S. Wrighton.....	149
High Energy Surface Reactions J. L. Margrave.....	176
Workshop on Ceramic Matrix Composites; H. K. Bowen, A. G. Evans, A. R. Cooper.....	185
1. Mechanical Response Considerations, A. G. Evans.....	190
2. Processing Considerations: The Matrix for Ceramic Fibers, H. K. Bowen.....	198
3. Modeling of Ceramic-Ceramic Composites, A. R. Cooper.....	207
4. Processing Ceramic Fiber Composites, R. W. Rice..	211
5. Past Experience with Non-Ceramic Matrix Composites, D. F. Adams.....	213
6. Synthesis and Application of $\beta$ -SiC Whiskers, J. V. Milewski.....	215
7. Properties of Nicalon Fibers and Composites, Tai-Il Mah.....	217
8. Ceramic Matrix Composites: Problems and Opportunities, T. Skinner and R. Banney.....	221
9. Fiber Reinforced Glass and Glass Ceramics, K. Prewo.....	224
Workshop on Metal Matrix Composites; R. Mehrabian and S. G. Fishman.....	233
1. Metal Matrix Composites: Plasticity, Fatigue and Transverse Cracking, G. J. Dvorak.....	241
2. Modeling Needs for Metal Matrix Composites, B. W. Rosen and K. Buesking.....	251
3. Interface Characterization of MMC, H. L. Marcus..	262
4. Sound Velocities and Elastic Constants in Two- Phase Solids: Measurement and Theory, H. M. Ledbetter and S. K. Datta.....	270

<u>TITLE</u>	<u>PAGE</u>
5. MMC Processing Considerations, K. M. Prewo.....	285
6. Metal Matrix Fabrication Processes: Advantages and Limitations, James Cornie.....	294
7. Interface Effects in Metal Matrix Composites, J. P. Hirth.....	304
8. Comments on Whisker Reinforcement of Metals: The Bonding Dilemma, A. G. Evans.....	306
9. Mechanics of Metal-Matrix Composites, B. Budiansky.....	307
10. Interfaces in Metal Matrix Composites, B. A. Wilcox.....	309
11. A Comment on the Limit to Fracture Toughness, D. C. Drucker.....	311
Workshop on Process Modeling and Control, --- R. Mehrabian, W. Isler and S. G. Wax.....	317
2. Case Study in Smart Processing of Ceramics; Development of a Model for Processing Monosized Powders, H. K. Bowen.....	381
3. Determination of Surface Chemical Composition and Stoichiometry, N. G. Eror.....	402
4. Powder Synthesis: Fundamental Aspects of Laser Driven Reactions, J. S. Haggerty.....	404
5. Use of Learning Systems for Current Ceramics Manufacturing, R. L. Currie.....	408
6. Opportunities for Acoustics in Ceramic Monitoring and Control, B. R. Tittmann.....	410
7. The Rapid Measurement of Temperature Distribution Within a Solid or Solidifying Body of Hot Steel, F. S. Biancaniello, R. B. Clough, M. Linzer, R. Mehrabian, S. J. Norton, L. R. Testardi, C. Turner and H. N. G. Wadley.....	415
8. Modeling of Metalworking Processes, H. L. Gegel..	439
9. In-Situ Process Monitoring and Control for Structural Components, M. J. Buckley, W. Pardee, F. Lange, M. Mitchell, and B. R. Tittman.....	455

TITLE

PAGE

10. Multilayer Films: Syntheses, Diagnostics, and Control, D. U. Gubser..... 462
11. The Peculiar Challenge of Chemical Processes to Advanced Control Systems, Rutherford Aris..... 468
12. Analytical Controls and Artificial Intelligence Experiences with Materials Processing Analogs R. L. Currie..... 472



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### Forword

This collection of papers does not constitute a formal reporting of the activities of the DARPA Materials Research Council Summer Conference. Each report, memoranda or technical note is a draft of the author or authors and is their work alone. The Steering Committee, in conjunction with the authors, will decide how this material can best be presented as a formal report to DARPA.



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## FACTORS GOVERNING YIELD OF GaAs INTEGRATED CIRCUITS

T. C. McGill, D. K. Ferry and H. Ehrenreich

### INTRODUCTION

Integrated circuits fabricated in III-V semiconductors have a number of advantages over Si based integrated circuits. These include increased speed for the same characteristic device dimensions<sup>1</sup>, lower power consumption, and enhanced radiation hardness<sup>2</sup>. The most advanced of the III-V technologies are those based on GaAs. These include technologies based on the metal-electrode-field-effect transistor (MESFET)<sup>3</sup> and junction-field-effect-transistor (JFET)<sup>3</sup> as well as the newer hetero-junction-bipolar transistor<sup>3</sup> and high-electron-mobility-transistor (HEMT)<sup>4</sup>.

DARPA is playing the leading role in pursuing the technology in this country involving levels of integration beyond small scale integrated circuits (SSI) and medium scale integrated circuits (MSI). Companies such as Hewlett-Packard and Tektronix have programs aimed at medium scale integrated circuits (MSI) which can be used in special purpose, high-speed instruments, and data acquisition and transmission systems. Discrete and very small levels of integration have been applied in the microwave region by a number of companies. Companies such as Bell Laboratories and IBM also have programs in this field. The program at IBM is reported to be increasing substantially in size.

Foreign competition in the area of GaAs integrated circuits comes most notably from efforts in Japan and France. The Japanese have announced some impressive successes including the development of a 1K bit random-access memory chip.<sup>5</sup>

Recently DARPA has embarked upon an ambitious and unique program to establish a single GaAs pilot production line. This pilot line will not only supply specific parts such as static random-access memories and gate arrays, but will also act as a GaAs foundry. This will allow groups in this country to take advantage of a facility that will be unique.

Until now all GaAs IC production in this country has been carried out in a research laboratory environment. In this environment the process is not defined uniquely enough to allow for a true test of yield and hence answer the basic question about manufacturability of GaAs LSI and VLSI.

Yield is a complicated, function of a number of interacting parameters. Some of the factors which play an important role are:

1. Complexity of integrated circuit design and tolerance of design to variation in performance of the elements.
2. Basic feature sizes.
3. Uniformity of basic materials used in the fabrication process.
4. Process control and uniformity.

Experience in the silicon industry indicates that attention to all these factors is required to produce a specific part with

a high yield in a given production facility. The GaAs pilot facility will allow the first meaningful test of the manufacturability of GaAs LSI under conditions in which attention has been paid to controlling item 4 above.

In this context the Materials Research Council organized a workshop to discuss what is currently known about GaAs IC yields and to attempt to identify future directions that may be important in developing circuits and fabrication processes which could increase yield.

## MEETINGS

### Presentations

The agenda for the meeting is given in the appendix along with a list of participants. In this section we will comment on some of the highlights of the meeting and note comments that are particularly relevant to our overall conclusion.

The first speaker at the meeting, R. E. Conklin, addressed the question of what we could learn from the VSHIC experience in producing new, high-performance chips. Conklin identified some key aspects of the Si manufacturing methodology that seem appropriate to GaAs IC production. These include the following guidelines: (1) "Document everything; (2) Measure, measure and measure; (3) Achieve a fixed process then change it only to resolve verified problems; (4) Allow time for initial equipment bugs and learning by people; (5) Run enough volume; (6) Force conservative designs; (7) Do systematic process and yield analysis."

R. Zuleeg from McDonnell-Douglas presented that company's yield analysis. He divided the yield loss into wafer losses, gross losses, and losses due to random defects. Wafer losses are due to wafer breakage. This factor should be relatively easy to eliminate. Gross losses are defined as disqualification of the wafer due to poor parameters, mask misalignment, etc., and losses due to random defects include sources such as conductor failures, vias, and material defects. As noted above yield is dependent upon sensitivity of a given circuit design to changes in the produced device parameters. At McDonnell-Douglas, calculations of the circuit sensitivity to variations in device parameters have been made using computer simulations of circuit performance. These simulations have provided information on the acceptable range of device parameters and provide a good quantitative mechanism of gauging the levels of process control that must be obtained to reach a certain level of yield. Sub-threshold leakage currents in devices and visible surface wafer defects ( $10$  to  $10,000 \text{ cm}^{-2}$ ), which could be due to wafer preparation, were identified as important areas of concern. Surface preparation could be very important, since unlike Si where oxidation and material removal are an integral part of the process, the devices are fabricated directly in the surface layer of the GaAs wafer.

The presentation from Rockwell was given by C. G. Kirkpatrick. Rockwell is also pursuing a program that is assessing the factors governing yield. Materials uniformity ques-



tions and the formulation of an adequate qualification procedure for substrates are being addressed. The sensitivity of some circuits requires considerable attention to the role played by these factors in device performance. For example, the standard Rockwell logic requires leakage currents to be as low as 1-10  $\mu\text{A}$  at a few volts for 5-10  $\mu\text{m}$  device spacing. However, the random-access-memory (RAM) devices require leakage to be held to 5-10 nA at a few volts for 3-4  $\mu\text{m}$  device spacing. Hence, the leakage current demands for RAM's are three orders of magnitude smaller than for logic. Since the electrical parameters are dependent upon the uniformity of the ion-implantation and annealing process, the capping and implantation process is receiving considerable attention. The uniformity of deposited films and processes for pattern definition was also identified as an important ingredient in determining yield. Kirkpatrick also indicated the need for a disciplined pilot facility to determine what yield could be reached.

The Hewlett-Packard program, as presented by R. A. Burmeister, is a quite different program. The major aims of the program is to fabricate SSI and MSI parts for commercial application in digital data acquisition and transmission. Acceptable yields (10-100%) have been obtained for these parts. The yields are consistent with a defect density of 100-400 defects per  $\text{cm}^2$  of active area on the chip<sup>7</sup>. One of the major points was the fact that the liquid encapsulated Czochralski (LEC) method results in a large number of dislocations ( $\sim 10^4 \text{ cm}^{-2}$ ). This dis-

location density should be compared with dislocation free Si that is currently used. The presence of dislocations in the LEC substrates could be very detrimental, particularly if lasers are to be fabricated on the substrate. Dark line defects associated with dislocations are a major mechanism for degradation in laser performance. New technologies such as heterojunction bipolar transistors and HEMT require epitaxial layers. The defect structures in these materials are not well understood at present.

R. Lee of Hughes Research Laboratories presented data on their experience with yield. At Hughes, the major concern is to develop high speed devices. Further, they are developing a technology that combines enhancement and depletion modes in a self-aligned gate technology. They consider the critical yield issues to be: Substrate materials uniformity, defects and surface preparation, lithography, pattern transfer, the properties of the transistor (including uniformity in threshold voltage and source-drain current), and control of proximity effects from nearby transistors.

J. Yuan of Texas Instruments presented their results on heterojunction bipolar transistors for gate arrays. Unlike the discussions by the previous speakers, the TI program requires the use of epitaxial layers since it involves not only GaAs but also GaAlAs. At TI, these epitaxial layers are prepared by molecular beam epitaxy (MBE). The unique yield issues associated with this program are connected with the need to control both

the layer fabrication and its properties in both GaAs and GaAlAs layers.

Bell Laboratories (R. Dingle) is concentrating on a number of different device technologies and applications. Most of their interests are in either SSI or MSI circuits which can be used in special purpose applications. They are using epitaxial processes to prepare material for the active device layer. The halide process for chemical vapor deposition of GaAs is used with a recessed gate device structure to fabricate standard microwave and SSI devices. Selectively-doped-hetero-structure transistors (SDHT or HEMT) are being fabricated in MBE layers. One major development at Bell Laboratories has been the successful growth of dislocation free GaAs (no further details are available). Their experience with yield is limited to SSI circuits and microwave devices where their yields are acceptable.

The Tektronix program, presented by A. Rode, includes the development of technologies for analog and MSI digital circuits. The emphasis is on high speed. The technology employs depletion mode FETS built in semi-insulating GaAs substrates by a recessed gate technology. Air bridge interconnections are used. Parts are available for prototyping with yields that are acceptable. A new process that will provide LSI digital circuits and precision analog circuits is under current development. Both enhancement and depletion mode FET's will be available. Parts such as 1K RAM's and 1K gate arrays are projected

for the 1985 time frame. In their opinion the major factors limiting yield are:

1. Materials - defects, substrate abnormalities, traps
2. Processing - passivation, lift-off, multi-levels of metallization, dielectrics in MIM structures.
3. Material/Process - backgating, isolation, in-process checks.
4. Device/circuit - design rules, circuit technology, non-uniformity of device parameters.

A major part of any yield analysis program is the testing of arrays of structures for defects and an analysis of the failure modes. M. Buehler (JPL) has designed test chips for silicon fabrication technologies. He is making similar designs for GaAs. The results of such studies should provide us with a mechanism to quantify various failure modes in GaAs integrated circuits.

#### DISCUSSION

Following the formal presentations, a number of brief informal presentations were made and a round table discussion to identify the key issues was organized.

Jim Gibbons (Avantek and Stanford) said that experience at Avantek indicated that the implementation of Si processing and manufacturing discipline could produce major improvements in GaAs yields for discrete devices and SSI fabricated on epitaxial layers. Gibbons is concerned about ion implantation as a basis for GaAs IC production since the implantation and anneal process

is likely to produce non-stoichiometric layers because of the compound nature of GaAs.

P. Solomon (IBM) made a number of points including the fact that for certain applications in military systems very small yields could be useful if the part is sufficiently unique. He indicated a concern that ohmic contacts could limit yield. All the yield analyses have made the assumption that device characteristics are distributed according to some simple distribution, typically taken to be Gaussian. However, Solomon noted that the actual distribution might be quite different, particularly for devices with large deviations in the values of their parameters. Since it is just these devices with large deviations in parameters that produce chip failures, it is important to have accurate values of the distribution for these more atypical devices.

R. Bauer (Xerox) indicated a need to continue to pursue epitaxial technologies, particularly MOCVD, both because of possible device advantages but also because of the fact that they are compatible with opto-electronics.

During the round-table discussion, a number of different subjects were identified for further study. The discussion centered about identifying areas where there may be unique problems in GaAs IC's as contrasted with Si. In the area of materials, the problems that were identified included:

- The role of dislocations<sup>8</sup>, defects<sup>9</sup>, and impurities<sup>10</sup> in determining device performance and yield.

- The properties of dislocation-free GaAs recently prepared at Bell Laboratories. Does it have the requisite materials parameters--high resistivity, resistance to thermal conversion, etc.?
- The usefulness of epilayers for device fabrication and the particular defect structure of the epilayer.
- The origin of wafer defects.
- The passivation of the surfaces and interfaces in GaAs.

In the area of device design, the major point was the close connection between yield and the design rules allowed in circuit design.

In the area of process development, the entire question of manufacturing process definition interacts heavily with yield. The techniques for ion-implantation, lift-off, ohmic contacts and requisite level of cleanliness were all identified as being important. The orientational effects of process induced stresses on device performance is an important issue.

The development of test chips was considered essential to identify clearly the source of yield loss.

#### Perspectives and Issues

The program to produce significant GaAs IC's is of national importance and implications transcending DOD's immediate needs. However, unlike the case of Si where the evolution of the complexity and performance of circuits has been gradual over a long period (approximately twenty years), the aim of the present program is to reach very complex circuits with small



dimensions very quickly in GaAs. In addition, GaAs design rules are beginning at a 1  $\mu$ m level, a level which Si will reach only within a few years. The success in manufacturing such chips depends in part on exploiting the knowledge of manufacturing techniques attained in the Si IC business and to identify which, if any, unique problems III-V semiconductors present.

The current successes in producing discrete devices, and small and medium scale integrated circuits at a number of individual organizations demonstrates that GaAs can in fact be manufactured with reasonable yields. However, the questions of whether chips with LSI and VLSI levels of integration can be manufactured have not been adequately explored. The current DARPA pilot program will test the question of manufacturability for one particular device technology for chips which have very demanding requirements. A failure to obtain high yield for these particular devices (16K SRAM's and 6K gate arrays) is only a test for one technology, one manufacturing process, and one set of structures. DARPA should consider the question as to whether the goals that have been set are attainable in the required time frame. Intermediate goals and other applications should be explored to evaluate the progress of the technology. For example, MSI circuits for high speed application could provide an intermediate target. Even today in the Si business the manufacturability of a given chip design is dependent on a number of factors that are neither fully understood nor predictable in a scientific sense. The successes of the pilot production

facility could well be attributable to the clear identification of some of the pitfalls of GaAs production.

Based on this meeting and our preceptions, we would recommend that DARPA emphasize a number of issues:

- (1) Encourage the development of pilot line experience with a number of different technologies (JFET, heterojunction bipolar, and HEMT.)
- (2) Allow a mix of chip designs and functions for GaAs chips to be pursued.
- (3) Adequately characterize yield failures to identify the mechanism responsible for difficulties.
- (4) Encourage imaginative, basic materials studies which will lead to a better understanding of the properties of GaAs (such as dislocations, EL2, carbon, etc.) and their connection with device performance.
- (5) Attempt to identify unique characteristics of GaAs such as surface passivation that could limit yield and initiate fundamental programs to address these questions.
- (6) In preparation for future technologies in this area, research on epitaxial systems and device structures should be pursued. These should include: molecular beam epitaxy, and chemical vapor deposition for preparation of layers, and novel device-relevant concepts.

#### ACKNOWLEDGEMENT

This report was written under the auspices of the DARPA Materials Research Council, Contract #MDA903-83-C-0349 with The University of Michigan.

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11. Recently the role of carbon or an impurity in GaAs has become the topic of some interest. See for example, A.T. Hunter, H. Kimura, J.P. Bauken, H.V. Winston, and O.J. Marsh, "Carbon in Semi-Insulating Liquid Encapsulated Czochralski GaAs" submitted to Applied Phys. Letters.

PROGRAM FOR MATERIALS RESEARCH COUNCIL MEETING  
ON  
FACTORS GOVERNING YIELD IN GaAs INTEGRATED CIRCUITS

July 6-7, 1983

Wednesday, July 6

R. Reynolds (DARPA)	Introductory Remarks
R. E. Conklin (Deputy Director VHSIC Program)	Manufacturing and Yield of VHSIC Chips
R. Zuleeg (McDonnell- Douglas)	Yield Modeling for GaAs IC's
C. G. Kirkpatrick (Rockwell)	Yield of GaAs IC's
R. A. Burmeister (HP)	GaAs Program at HP
C. F. Krumm (Hughes)	Yield of GaAs IC's at Hughes
J. Yuan (TI)	Yield at TI
R. Dingle (BL)	Yield at Bell Laboratories

Thursday, July 7

A. Rode (Tektronix)	Yield Results at Tektronix
M. G. Buelher (JPL)	Pin Hole Detection for Yield Analysis
Discussion and Summary	

ATTENDEES  
YIELD IN GaAs CIRCUITS

July 6-7, 1983

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D. Ferry	CSU/MRC
H. Wieder	UCSD
R. Bauer	Xerox
A. Rode	Tektronix
R. Osgood	Columbia
J. Margrave	Rice/MRC
S. Wax	DARPA
R. Burmeister	Hewlett-Packard Labs
R. Lee	Hughes Research Lab
G. Vineyard	MRC
J. Hirth	MRC
M. Sinnott	MRC
R. Conklin	WP AFB
R. Reynolds	DARPA
R. Dingle	Bell Labs
A. Yariv	Caltech/MRC
F. Patten	DARPA
M. Buehler	WPL

## THREE DIMENSIONAL INTEGRATED CIRCUITS

D. K. Ferry, T. C. McGill, and H. Ehrenreich

### INTRODUCTION

The continued push to ever smaller semiconductor devices and the concomitant increase in density in integrated circuits has pushed lithographic line definition down toward the  $1.0\text{ }\mu\text{m}$  design rule range for NMOS Si. Other technologies, such as CMOS are utilizing design rules only slightly larger. As device dimensions are reduced, it becomes possible to pack more devices on a chip, thus achieving higher integration levels, and to operate the devices at a higher speed. However, this has pushed the actual devices to dimensions that are sufficiently small that their operation has begun to deviate from the performance associated with simple long-channel devices. The onset of second-order effects, such as gate-drain charge sharing or interconnection stray coupling, are sufficiently significant that they are presently conjectured to limit MOS technology to design rules larger than  $0.5\text{ }\mu\text{m}$ .

Because of the above problems, attention has turned to three-dimensional integration (3DIC). In this approach 3DIC devices are produced in multi-layers on a single wafer. For example, a second Si layer is grown over the field oxide and used for the second level of devices. This layer is typically either epitaxial silicon or recrystallized polysilicon. By use of such techniques, it is conceivable that the packing density can be increased for an additional one to two generations of chips



without exceeding any currently anticipated design rule limitations.

In view of the possible future importance of 3DIC chip designs, the MRC organized a meeting on July 7-8, 1983, devoted to a general discussion of materials, devices, and architectures that might be used as the technology develops. The considerations of this meeting are intended to form a basis for assessing the promises and problems of this technology and to focus on some of the key development issues.

The following summary presents a synopsis of the various presentations and discussions. This is followed by general observations about the status and recommendations about the future of the field. A program and list of attendees concludes the report.

#### MEETING HIGHLIGHTS

The session began with a discussion by J. Gibbons (Stanford) of the general principles of folding and rotation of the planar device layout that is used to achieve the stacked configuration in CMOS. Many of the ideas used to design CMOS devices are extensions of silicon-on-insulator technology. Among the types of folding, one that is generally used involves placing the p-channel pull-up device above the n-channel device in such a manner that a common gate is utilized. This is called stacked CMOS. One point, well illustrated in his talk is that device and circuit design remains in the "custom" layout mode since no circuit standardization has yet been achieved. He

emphasized that 3DIC has the greatest likelihood of success in applications where (1) only a small number of masks or additional masking steps are required, (2) the device density is of great importance and (3) device properties not obtainable in bulk or SOI are important. Another general conclusion is that the three dimension structure does not produce any great increase in speed. He has proposed a general figure-of-merit, given as

$$\text{FOM} = (\text{yield})^{\text{Mask Count}} / \langle 2 \times \text{delay} \times \text{area} \rangle,$$

which indicates quantitatively that care must be taken not to introduce a significant increase in the number of mask levels. Thus, 3DIC's may be limited to dense memory, or possibly bipolar applications.

J. Grinberg (Hughes) gave a presentation on system considerations underlying the "ultimate" multi-level 3DIC. Such structures are most useful in fully parallel configurations involved, for example, in array or image processing. Since digital technology offers the possibility of programmable interactions between image planes (layers), 3DIC's might be promising in this area. The CMOS RAM was regarded as the major near-term opportunity for 3DIC.

E. Maby (MIT) discussed the two level integration being studied in his laboratory. Again, the investigation centers on stacked CMOS, but utilizing a fully self-aligned approach. This approach, however, may require more masking levels. In the MIT

studies this need is partly accounted for by their study of quite larger devices.

P. Sullivan (NCR) discussed the programs being pursued by NCR in the areas of 3DIC and arrays of processors. Using a 4  $\mu\text{m}$  CMOS process, they have produced a 3x6 array of elemental, bit-serial binary processors. Each processor contains a 1 bit ALU, 4 registers, and 128 bits of memory. The array is programmed by 13 control lines and seven address lines. It is, therefore, capable of full cellular computation within this limited size. Thus, this array forms a basis for some of the systems discussed earlier by Grinberg. Future plans call for a 72 element array.

NCR has also fabricated a stacked CMOS implementation of 3DIC which required 8 masking levels, although the devices had 7-10  $\mu\text{m}$  channel lengths. He also reported on collaborative work with G. Collins (Colorado State University) in which pulsed lasers and e-beams are being used for laser enhanced CVD and annealing. However, the pulsed sources remain a serious drawback for application to processing in 3DIC's.

B. Hoeflinger (University of Minnesota) discussed collaborative work with Honeywell. This work emphasizes low temperature epitaxy as an alternative to laser/thermal recrystallization. Their stacked CMOS process utilizes only 7 masking levels.

H. W. Lan (Texas Instruments) gave an overview of TI's efforts at 3DIC. Again, this involved the implementation of a

stacked CMOS static RAM. Here, 4 and 8  $\mu\text{m}$  channel lengths were being used for the n-channel and p-channel devices, respectively. In addition to laser recrystallization, TI has also utilized hydrogenation to passivate grain boundaries in the imperfectly recrystallized second layer. Ian also raised a question about the compatibility of laser processing with current Si processing technology.

G. Cellar (Bell Labs) discussed their efforts on recrystallization from a local melt, in which the entire upper polysilicon layer is heated at one time using rapid thermal annealing with tungsten lamps. In this way, epitaxial regrowth of the upper layers, rather than recrystallization from the polycrystalline form is achieved. He has found that if the film is thick (length/thickness =  $L/d < 100$ ), then grain sub-boundaries are not a problem.

M. Geiss (Lincoln Labs) summarized that group's efforts on recrystallization using a strip heater and low temperature epitaxy.

Finally, R. Osgood (Columbia) discussed the use of laser-driven etching. This process provides high anisotropy due to the preferred direction of the light beam combined with high resolution. He demonstrated the application of via hole drilling. The process itself has a weak threshold effect. In the low power regime, photo dissociation of the HCl etchant is predominant, while thermal dissociation dominates the high power region.

## HIGHLIGHTS OF THE DISCUSSION

An informal group discussion followed the presentations. The general consensus seems to be that the short term applicability of 3DIC is limited to increasing the packing density in static RAM, particularly CMOS. On the longer time scale, this technology should become more useful, particularly as design rule limits begin to halt further reductions of feature size in conventional technology. However, almost all investigations have been limited to stacked CMOS, where the circuit is obvious; little effort has been expended in NMOS, or other technologies. Neither have there been any attempts to incorporate such devices in new computer architectures. (This leads to a curious "Catch 22" situation: a designer of a new IC component will not perfect the device until it is needed in a computer architecture; conversely, an architect will rarely use a hypothetical device in a design.)

There is a significant problem vis-a-vis the second level of device material. The quality of the recrystallized semiconductor material is not particularly good. This appears not to be critical in stacked CMOS, where speed has not been a major consideration to date. There is also concern as to whether multi-level circuitry can withstand the high temperature processing inherent in recrystallization. While a low temperature epitaxial regrowth of the upper layers would appear to be more advantageous, current efforts in this direction are limited. The possibility of using materials other than silicon, such as GaAs, in the upper layers was also discussed.

Problems connected with the interlayer capacitance and lithographic alignment suggest that technology relying on self-alignment would be preferable. This becomes particularly important as design rules are reduced toward 1.0  $\mu\text{m}$ . Planarization required by photolithography is also a problem. There was considerable discussion as to whether non-planar approaches could be found and to whether alternative upper layer materials would prove useful.

Finally, there were some questions as to whether the use of larger die size in normal two-dimensional IC's (requiring improvement in defect control or redundancy in design) would increase the integration and reduce the need of success for 3DIC. While there was no consensus, there was a feeling that although this was true in the near term, constraints on the design rules would require both two- and three-dimensional approaches in the long term.

#### SUMMARY

The area of 3DIC's requires continuing attention, in part because it holds promise for continuing the increase in packing density. However, the current approaches toward this developing technology appear to have uncovered as many problems as they have answered. Outside of NCR's modest effort, it appears that the entire program is supported by DOD and the Semiconductor Research Cooperative. This is probably appropriate and befitting the speculative nature of the research. Unfortunately, the various programs seem to be concentrating too

much on the intuitively obvious stacked CMOS, rather than on creative approaches that could take advantage of the more diverse structure made possible by 3DIC's.

The presentations and discussion highlighted several important questions which should be addressed in future research programs.

- Can recrystallization ever provide the reproducibility necessary in a production environment? This is particularly pertinent in laser and pulsed source modes of recrystallization. Moreover, can the lower levels of already delineated devices withstand the high temperatures required for recrystallization?
- Is the material quality of upper levels adequate to provide performance levels sufficient to make 3DIC's worth pursuing? The development of device concepts beyond stacked CMOS, in particular, would require quality well beyond that currently being achieved.
- Are current efforts limiting the quest for novel system structures, e.g., digital/optical interface devices, because of insufficient input from computer architects?
- What thermal limitations in 3DIC can be expected from the multiple interfaces introduced in this structure?

#### ACKNOWLEDGEMENT

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PROGRAM FOR MATERIAL RESEARCH COUNCIL MEETING  
ON  
THREE DIMENSIONAL INTEGRATED CIRCUITS

July 7-8, 1983

Thursday, July 7

R. A. Reynolds (DARPA)	Introductory Remarks
S. Roosild (DARPA)	
J. Gibbons (Stanford)	Three Dimensional IC's
J. Grinberg (Hughes)	Systems Considerations for Three-Dimensional IC's

Friday, July 8

E. Maby (MIT/RPI)	3D-IC's at MIT
P. A. Sullivan (NCR)	Three-Dimensional CMOS Technologies at CSU & NCR
B. Hoeflinger (UM)	Three-Dimensional CMOS Technologies
H. W. Lan (TI)	Technologies for Three Dimensional IC's
G. K. Celler (BL)	Silicon on Insulators by Crystallization from the Melt
M. Geiss (Lincoln Labs)	Three Dimensional IC's
R. Osgood (Col.)	Etching for 3D-IC's
Discussion and Summary	



ATTENDEES

THREE-DIMENSIONAL INTEGRATED CIRCUITS

July 7-8, 1983

<u>Name</u>	<u>Affiliation</u>
S. Roosild	DARPA
D. Reynolds	DARPA
J. Plummer	Stanford/MRC
J. Gibbons	Stanford
P. Sullivan	NCR Microelectronics
H. Ehrenreich	Harvard/MRC
J. Harris	Stanford
T. McGill	Caltech/MRC
D. Ferry	CSU/MRC
J. Hirth	OSU/MRC
G. Vineyard	BWL/MRC
G. Celler	Bell Labs
H. Lan	Texas Instruments
R. Osgood	Columbia
T. Barbee	Stanford University
M. Wrighton	MIT/MRC
A. Yariv	Caltech/MRC
R. Zuleeg	McDonnell Douglas
M. Geis	Lincoln Labs
G. Davis	Naval Research Lab
E. Maby	RPI
S. Wax	DARPA
J. Neff	DARPA
E. Levinthal	DARPA
J. Grinberg	Hughes
H. Wieder	UCSD
B. Hoeflinger	University of Minnesota

## MONOLAYER AND MULTILAYER THIN FILM MATERIALS

M. S. Wrighton

The techniques of Langmuir and Blodgett can be used to prepare monolayers and multilayers of organic materials on a variety of substrates.<sup>1</sup> The films of organic materials formed by the LB techniques can be quite thin ( $<30\text{\AA}$ ). The molecules in such films can be oriented. In principle, uniform monolayer and multilayer films can be deposited over very large areas. Thin, highly organized, and large areas are characteristics of LB films that have been known for 50 years, but there is presently renewed interest in these materials. The interest stems from the possibility that significant applications unique to LB films are possible.<sup>1,2</sup> Some of the possible applications noted in recent years are given in Table I. Many of the applications are of direct interest to the DARPA/DSO and a program in the area of LB films is to be undertaken. A workshop on LB films was held at the MRC meeting on July 13 and 14, 1983 to bring together experts in the field, to learn about new results first hand, and to air research problems, results, and opportunities.

### MEETING SUMMARY

The meeting agenda and participants list are given at the end of this report. M. Wrighton of the MRC organized the meeting in consultation with R. Reynolds of DARPA.

The first speaker, G. Roberts, University of Durham, gave an overview of his research of LB films with an emphasis on

TABLE I. Tantalizing Possible Applications of LB Films

MISFET Devices with InP, GaAs

Large Area Displays

Chemical Sensors

Josephson Junctions

Photovoltaic Devices

Waveguides

IR Detectors

Electron Beam Resists

applications in electronic devices, including electroluminescent devices, MIS devices, and H<sub>2</sub> and NO<sub>2</sub> sensors. Roberts raised important issues such as the fact that multilayer film structure is substrate dependent and indicated that single crystal substrates (GaAs, Si, InP) give better order in the multilayer than does an amorphous material such as amorphous Si. The dipping rate for the formation of LB films was said to be acceptable for technological applications. Roberts emphasized the use of new phthalocyanines in thin film assemblies as these are very robust molecules that have some unique properties. In several key areas Roberts was non-specific, owing to proprietary interest in the findings, e.g. GaAs MISFET and IR detectors.

G. Gaines of GE began his presentation with a brief historical review of LB film research at the GE R & D Center where Langmuir and Blodgett did their classic work. Gaines indicated that he is interested in reentering the field after some years of inactivity. He surveyed some the the consequences of aging, deposition procedures, etc., on film structure and indicated an interest in pursuing a program to study LB deposition of polymers such as  $(-N-P(OCH_2CF_3)_2-)_n$  (a polyphosphazene), polyacrylonitrile, and polyvinylcarbazole. Some advantages of depositing pre-formed polymers include the fact that the polymer layers can be ultra-thin ( $<10\text{\AA}$ ), they can have high thermal and mechanical stability, stresses due to polymerization of a monolayer or a multilayer of monomers can be avoided, and there is a wide variety of polymers that can be investigated.

J. Rabolt of IBM, San Jose, presented IBM's results relating to the characterization of LB films by vibrational spectroscopic techniques. Emphasis was on fatty acids to establish a firm basis for the vibrational spectroscopic techniques being developed to obtain structural information relating to orientation of molecules. Raman spectroscopy and FTIR spectroscopy were both employed in the characterization procedures. IBM's future basic research program includes investigation of temperature effects on LB films (including phase transitions, 2-D melting and annealing) and syntheses of novel monolayer components. Justification of the IBM effort on practical grounds include the following: adhesion, lubrication, magnetic organization, second harmonic generation, e-beam lithography, insulation, and encapsulation.

A major new research initiative in LB films at Case Western was presented by S. Rickert. The program is to be a broadly based effort to investigate new ways to prepare LB films for device applications. The research is to be undertaken in a new laboratory called the Polymer Microdevice Laboratory that is to be an interdisciplinary research facility involving chemists and electrical engineers.

F. Pease of the Stanford Electronics Laboratory discussed e-beam resist requirements for VLSI and presented results of a collaborative effort with A. Garito on the use of polymerized LB diacetylene films as an e-beam resist. The results with the polymerized LB films were encouraging inasmuch as the films

survived the transit between laboratories and yielded fairly good results. Demonstrated resolution was not as good as results of Barraud. Pease did demonstrate that the resist withstood  $\text{CF}_4/\text{O}_2$  plasma etch treatment. Defect density in the resist was an issue of considerable concern.

H. Wohltjen of NRL outlined the present effort in LB films at NRL. The two programs are experimental studies of chemical sensors and theoretical consideration of molecular electronics. The advantages of LB films in the sensors were identified as the fact that very thin, uniform films could be made from a wide variety of materials that rapidly equilibrate with sample vapors. The devices under study include surface acoustic wave devices, optical waveguides, and microelectrodes.

The research activities at Saclay in France were discussed by A. Barraud. He emphasized their applications oriented research on biomimetic devices and e-beam resists. The amount of research done beyond that in the literature has been small, owing to a rebuilding effort. Work reviewed in previous MRC reports regarding  $\omega$ -tricosenoic acid as a negative resist was summarized: high sensitivity ( $0.5 \mu\text{C}/\text{cm}^2$  at 5kV), high contrast ( $\gamma=3$ ) and high resolution (1000 Å actually obtained after etching using a 400 Å beam spot). The future effort at Saclay will likely be directed toward structural characterization of well-prepared films.

A. Garito described part of his research program underway at the University of Pennsylvania. Of most relevance to the

workshop were his structural studies of polymerized diacetylene multilayers. The data showed better order for the diacetylene multilayers than for the classic arachidate multilayers.

J. Lando of Case Western also described work relating to the polymerization of monolayers. Lando described work in a variety of areas including the use of LB films as the insulator in Josephson junctions with a 100% success rate for working devices.

S. Tripathy of GTE Laboratories summarized their two-year effort in the LB film area. The GTE effort concerns the use of polymerized diacetylene films for use in optical devices.

The workshop concluded with a presentation by G. Roberts of the functions of the Molecular Electronics Discussion Group (MEDG) of the United Kingdom Science and Engineering Research Council. The MEDG coordinates interdisciplinary research related to the use of molecular components in devices. One working party is on LB films, another concerns biotechnology for sensor applications, and the third involves electroactive polymers.

#### ASSESSMENT OF THE FIELD OF LB FILMS

The workshop revealed that the field of LB films is one that is scientifically stimulating and where potential applications are interesting. At the present time there are no practical applications of real consequence, though some preliminary results on several fronts indicate that LB films may serve a

unique function in some situations. In this regard the applications that are most intriguing in the near term are e-beam resists, chemical sensors, and LB films as insulators in various MIS or MIM structures. However, for the most part, the area of LB films must be regarded as a basic science area where major advances in fundamental knowledge are necessary before there can be a technology. Some of the key areas requiring study are set out in the sections that follow.

#### Monolayer and Multilayer Structures

One of the touted properties of LB films is the ability to make assemblies of organized molecules. In the broad sense this is an established fact, but many structural issues crucial to applications remain unresolved. A sample of the structural problems that exist are:

- (a) Role of Substrate Structure - does an ordered substrate substantatively improve the quality of LB films?

Roberts' results are ambiguous in this regard though he notes a correlation of crystallinity of LB multilayers with the use of single-crystal substrates. The ambiguity arises because many single crystal surfaces dipped in liquid  $H_2O$  have an amorphous surface layer depending on the surface chemistry with  $H_2O$ .

- (b) Defect Density - in many applications the structural uniformity of the multilayer assembly is of importance. There has been relatively little effort devoted to determining the defect density, the nature of defects, and



their consequence on properties such as waveguiding, diffusion of gases, and conductivity. The following report by J. P. Hirth details some possible defect types.

- (c) Effect of Surfactant Structure - many of the interesting applications involve the use of novel molecules. What are the structural consequences when using a diversity of molecular types?
- (d) "Superlattices" - LB film synthesis could be regarded as the chemists' MBE. Superlattices can be synthesized, in principle; what are their properties?
- (e) Aging and Annealing - what is the long term structure of the multilayer assembly? Does H<sub>2</sub>O in the films, or at the substrate/multilayer interface change the structure and does the H<sub>2</sub>O content change with time? Some multilayers adopt thermodynamically stable structures; can metastable structures exist for long periods of time and what is the temperature dependence of the changes in structure that could occur?

#### Interfacial Properties

Applications of LB films involve deposition onto active substrates. In some cases the applications involve metallization. For example, in a MISFET the deposition of the LB film on the semiconductor as the insulator is a gentle procedure, but there are indications that the barrier height can be changed. What is responsible for the change in barrier height? What is the metallization chemistry? This issue would seem to be criti-

cal for situations where the insulator is one molecular layer thick and even more so for the ultrathin ( $<10\text{\AA}$ ) polymer layers. The application of state of the art surface science tools should prove fruitful in addressing some of these issues.

#### Multilayer Fabrication Techniques

There are preliminary results that show that fabrication of multilayers can be sufficiently fast to meet technological demands. However, there are many issues in this regard that remain to be addressed. Among the areas of concern might be the question of whether multilayers can be fabricated using troughs containing liquids other than  $\text{H}_2\text{O}$ . The physical dimensions of high quality films will be a major issue. The environment in which the films are grown may also have profound practical consequences. The environmental variables include the gaseous atmosphere above a trough and the particulate contamination.

#### Unique Molecules

A key, perhaps the key, to applications of LB films is the ability to synthesize molecules that will have the desired properties. For example, in the area of chemical sensors the films must respond uniquely to species in the environment. For e-beam resists there must be polymerizable functionality. Molecular synthesis is often a labor intensive effort compared to testing and evaluation. Synthesis of surfactants is not an area pursued actively by the most creative chemists. Access to the specialty chemicals will be crucial to any program. It is also possible that the purity of such reagents will have to be

superior to that ordinarily deemed acceptable for most purposes in chemistry.

#### Multilayer Properties

Aside from structure there are many properties of LB films that are of fundamental and practical interest. Some of the properties, of course, will be those associated with the molecular building blocks, such as optical absorption. Others will be controlled by the product(s) of reactions of the molecular units after the LB film is in place as in e-beam resists. Reactivity, long term integrity, gas permeability, and mechanical properties of LB films are of interest.

#### CONCLUSIONS

LB film research is an exciting scientific endeavor that may lead to some significant applications of importance to DARPA. For now the applications must be regarded as future opportunities. The program to study and evaluate LB film must be regarded as long term inasmuch as it may take two to three years from a start-up operation to achieve state of the art sophistication. Some of the research such as organic synthesis will be labor intensive, while other parts will require surface science expertise at the state of the art. Much of the activity will require a willingness to interact with a broad spectrum of disciplines, especially in those programs where practical applications are to be evaluated.

#### ACKNOWLEDGEMENT

This report was written under the auspices of the DARPA Materials Research Council, Contract #MDA903-83-C-0349 with The University of Michigan.

#### REFERENCES

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2. Cf. Thin Solid Films, 99, (1982) from the proceedings of the International Conference on Langmuir-Blodgett Films held in Durham, England, Sept. 1982.

MATERIALS RESEARCH COUNCIL

WORKSHOP ON LANGMUIR-BLODGETT AND THIN FILM MATERIALS AND  
ELECTRONIC DEVICE APPLICATIONS

July 13-14, 1983

July 13

Welcome and Introduction, M. S. Wrighton, MRC and MIT

DARPA Interests, R. A. Reynolds, DARPA

"Overview of the Possible Applications of Langmuir-Blodgett Films", G. Roberts, Univ. of Durham

"Langmuir-Blodgett Film Research at GE", G. L. Gaines, GE R&D

"Langmuir-Blodgett Film Research at IBM", J. F. Rabolt, IBM-San Jose

"Langmuir-Blodgett Film Research at Case Western Reserve University", S. Rickert, Case Western Reserve Univ.

"Application of Langmuir-Blodgett Film as a Photoresist", F. Pease, Stanford Electronics Lab.

"LB Film Research at NRL", H. Wohltjen, NRL.

July 14

Applications of Langmuir-Blodgett Film, Dr. Andre Barrand, Centre d'Etudes Nucleaires de Saclay, France

"Recent Results at the University of Pennsylvania", T. Garito, Univ. of Penn.

"Interesting Applications of Langmuir-Blodgett Films", J. Lando, Case Western Reserve Univ.

Discussion of Opportunities for DARPA in Langmuir-Blodgett Film Research - All participants.

"Overview of Molecular Electronics Study Group in the United Kingdom", G. Roberts, Univ. of Durham

"Non-Linear Optical Properties of Langmuir-Blodgett Multilayers of Polydiacetylene", S. Tripathy, GTE Labs.

ATTENDANCE LIST

WORKSHOP ON LANGMUIR-BLODGETT AND THIN FILM MATERIALS AND  
ELECTRONIC DEVICE APPLICATIONS

July 13-14, 1983

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R. Reynolds	DARPA	
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C. Hicks	NOSC	619-225-6495
T. Jones	NOSC	619-225-6871
H. Wieder	UCSD	619-452-3546
G. Roberts	Durham	

# LINE DEFECTS IN LANGMUIR-BLODGETT FILMS

J. P. Hirth

## INTRODUCTION

In bulk crystals or in overgrowths of metals or inorganic compounds, the line and surface defects are characterized in terms of simple dislocations, grain boundaries composed of such dislocations, and planar faults: stacking faults and twin boundaries. L-B films, in particular monolayer films, can be thought of as two-dimensional crystals. They too can contain simple dislocations with a defect size characterized by atomic spacings, say of the length of a carbon-carbon bond. However, other defects can exist with characteristic lengths equal to one or two layer thicknesses. In the following discussion, the various defects are classified.

## DEFECT TYPES

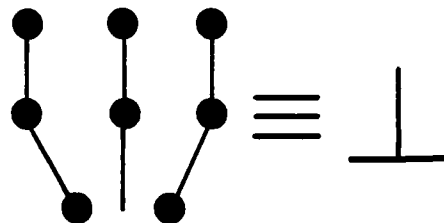
### "Normal" Defects in 2-D Crystal

Figure 1 presents a view of simple dislocation and planar defects in an L-B monolayer. These defects are equivalents of bulk defects in metals or in, say, polymer crystals. The Burger's vectors of the dislocations are equal in length to the lattice parameter of the 2-D crystal. These defects can arise either during film formation or by deformation.

### "Normal" Interface-Type Defects

Figure 2 shows other standard types of defects. The L-B film may form in an epitaxial orientation with respect to the

a.



b.



c.

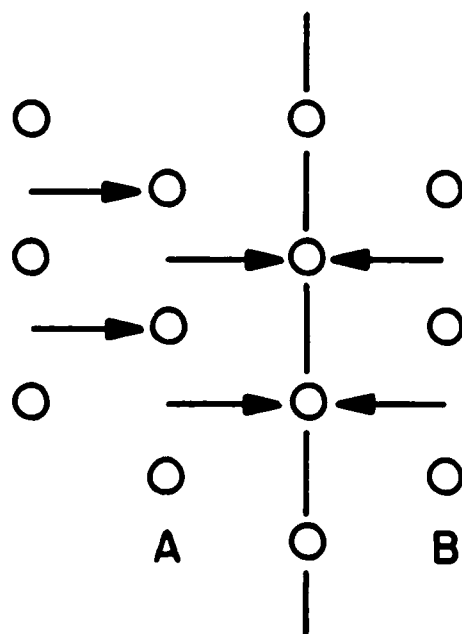


Figure 1. Projection normal to surface showing defects in 2D crystal.

- a. Edge dislocation in lattice with dots representing molecular chains and symbol equivalent.
- b. Grain boundary composed of edge dislocations.
- c. Triangular lattice with polarity A or B represented by arrows and dashed line representing a twin boundary.



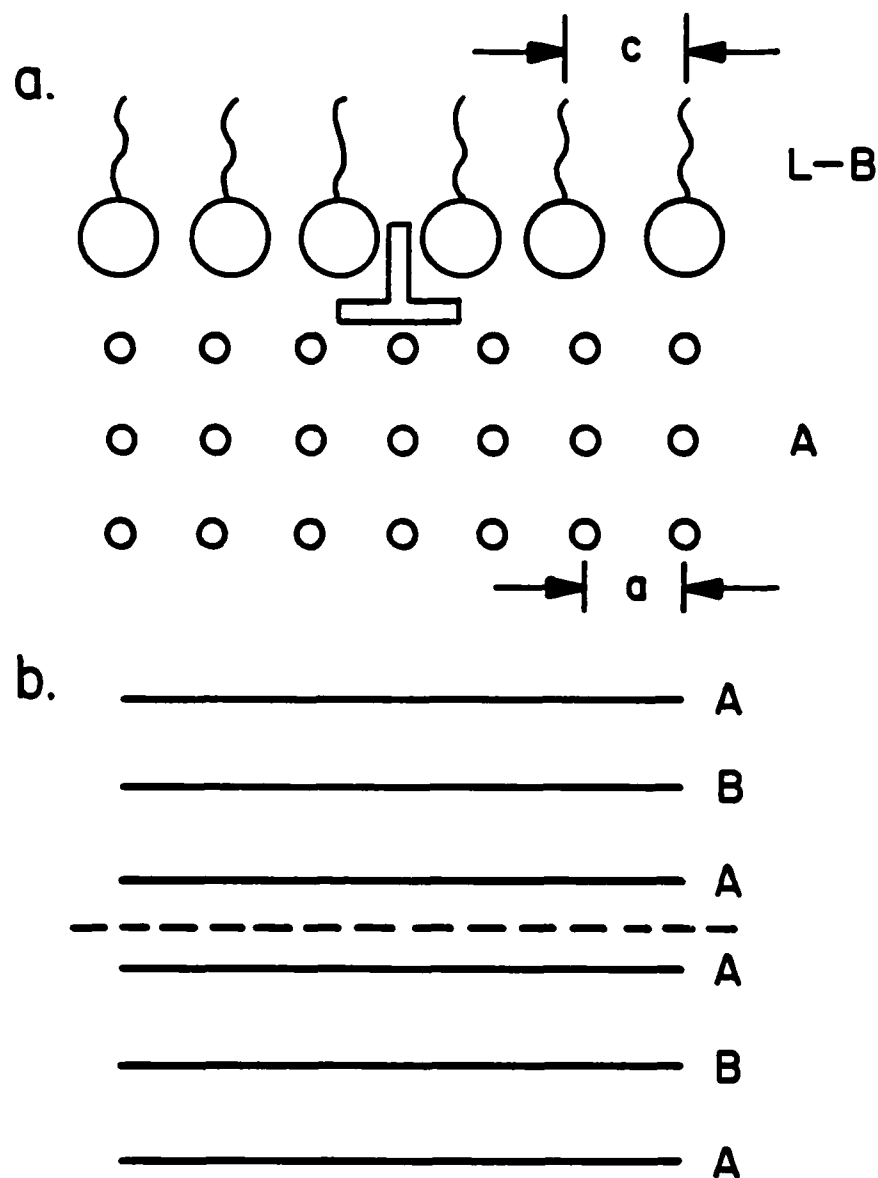


Figure 2. Projection Parallel to Surface.

- a. Interface dislocation at interface between L-B film and substrate A.
- b. Stack of L-B layers with polarity A or B as in Fig. 1c with stacking fault represented by dashed line.

substrate. If so, its lattice parameter  $c$  will in general differ from that,  $a$ , of the substrate. Because of the relatively weak binding between the film and the substrate it is unlikely that the lattices would be coherent with attendant coherency strains. It appears more likely that the strains would be relaxed by interface dislocations as in Fig. 2a. Also, in multiple L-B films which have polarity or low symmetry in their 2-D crystal structure, stacking faults are possible as shown in Fig. 2b. These defects would be growth defects.

#### Superdislocations

Superdislocations have Burgers lengths  $b$  related to the thickness  $h$  of a L-B layer. Figure 3 illustrates superdislocations. Figure 3a shows a fold-type edge dislocation with  $b=2h$ . Since the head-tail polarity is reversed at a fold, a stacking fault will be associated with this defect as indicated by the dashed line if the L-B film has such polarity. Figure 3b shows an edge dislocation and Fig. 3c a screw dislocation. For crystals with in-plane polarity such as that shown in Fig. 1c, the dislocations in Figs. 3b and 3c could also have associated stacking faults as illustrated for the example of Fig. 3b. These defects again would most likely be growth defects.

#### Defects Associated with Substrate Steps

Figure 4 illustrates defects associated with substrate steps. The bending of an L-B film grown over a step creates a strain field equivalent to an edge superdislocation as shown by a comparison of Fig. 4a and 3b. The defect in Fig. 4a is

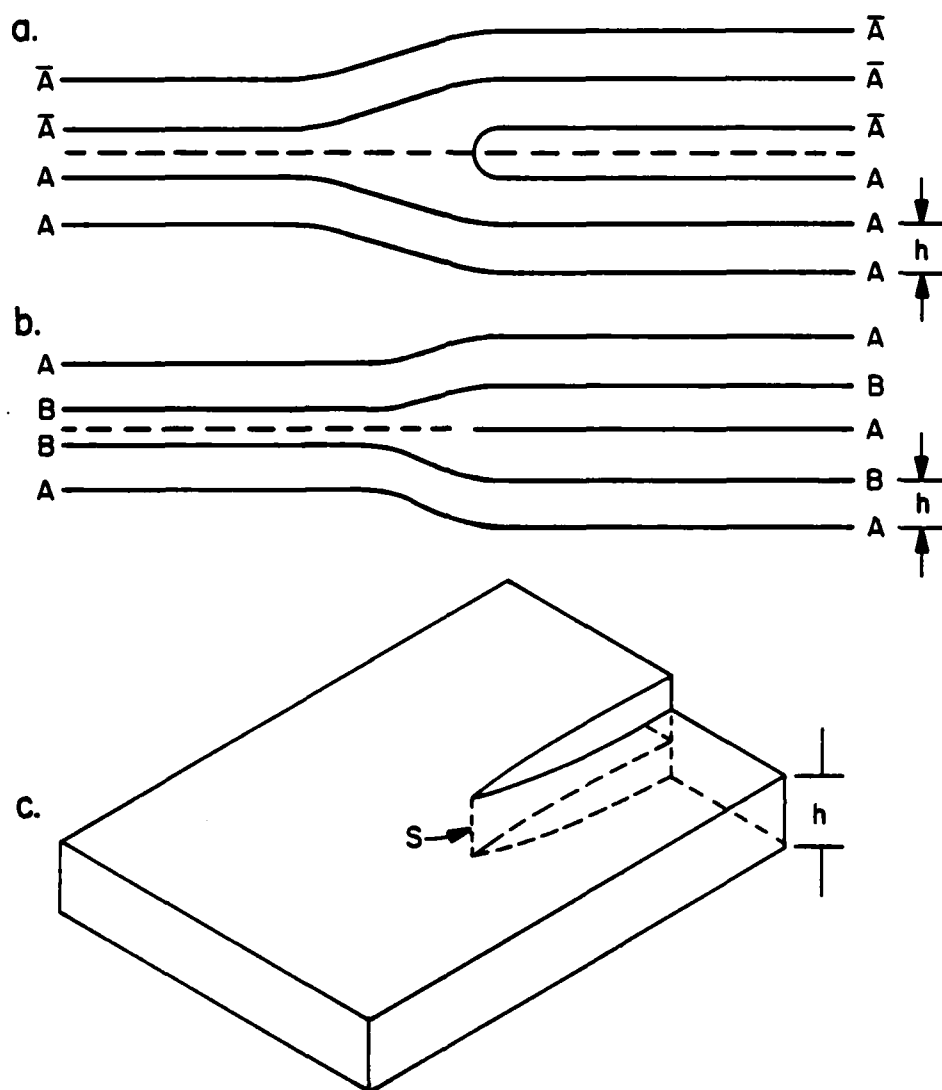


Figure 3. Superdislocations

- a. Fold-edge dislocation and associated stacking fault (dashed line); A represents inverted A layer.
- b. Edge dislocation and associated stack fault (dashed line).
- c. Screw dislocation S.

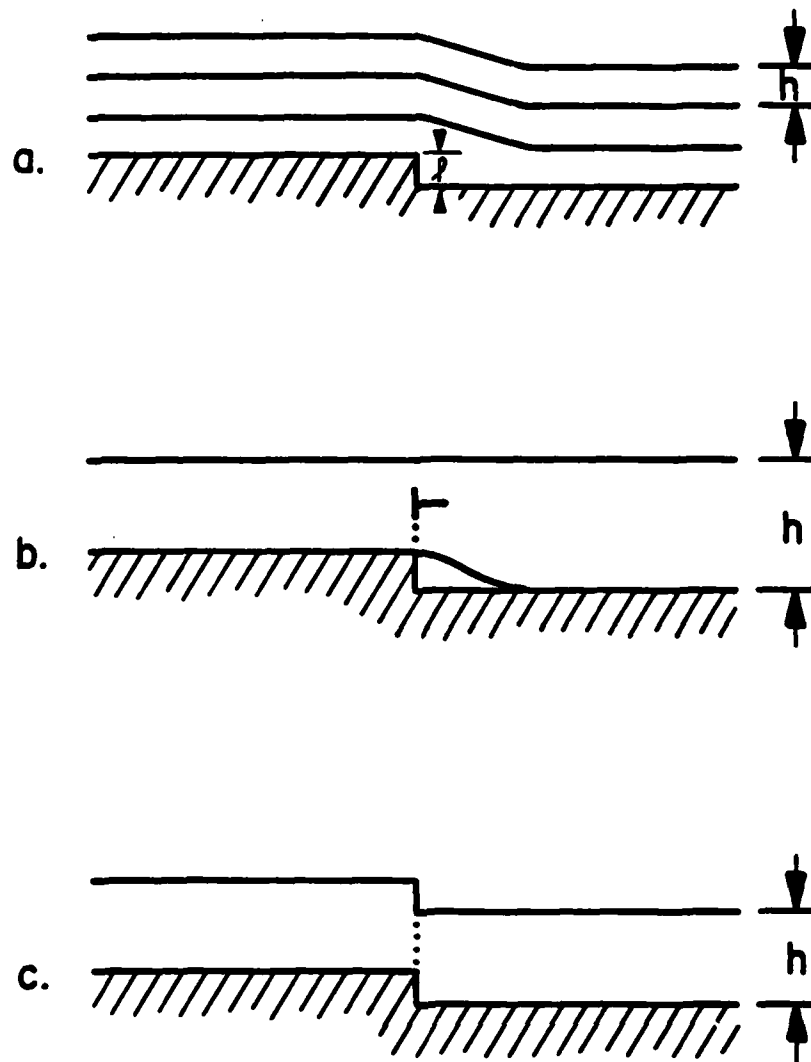


Figure 4. Defects associated with steps in substrate.

- a. Partial superdislocation of edge type.
- b. Edge dislocation and associated stacking fault.
- c. Stacking fault.

equivalent to an edge dislocation with  $b=2l$ . Since  $l$  is unequal to the regular L-B spacing  $h$ , the dislocation, in the formal language of such defects, would be called a partial dislocation. Upon aging or after growth, the strain field could be relaxed as shown in Figs. 4b and 4c. For small steps, a simple dislocation with  $b$  equal to an atom spacing in the chain could form as shown in Fig. 4b. Except for highly symmetric structures, such a dislocation would also have a stacking fault as indicated in Fig. 4b. The dislocation could move through the L-B film as in Fig. 4c, but could still leave a fault behind.

"Point" defects such as kinks and jags in the dislocation lines, vacancies, interstitials, and twists in the chains that can be described as disclinations as discussed in the polymer literature can also exist. These are not discussed here.

#### SOME IMPLICATIONS

Almost all substrates now used for L-B films have surface roughness of the scale of 10nm or more. Thus, the defects shown in Fig. 4 must, in general, be present. The other defects could arise as a consequence of growth accidents during film formation in the bath, growth or deformation accidents during transfer to the substrate, or deformation or relaxation subsequent to transfer. The defects obviously impair film perfection. The defects could detract from conductivity; act as traps for electronic carriers or recombination centers, act as surface states; carry fixed charge, and the like; and provide "leaks" for diffusion of atoms, molecules or ions. Evidently, these

defects would degrade the properties of L-B films in a variety of applications.

Except for grain boundaries and twin boundaries, the defects would not be detectable by the LEED or HEED electron diffraction techniques that are now used to characterize L-B films. The defects with associated irregularities at the surface of the L-B film could be studied by replica-transmission electron microscopy. Better, all of the defects could be resolved directly by transmission electron microscopy. A thin substrate (~100nm) could be grown on a backing crystal, the L-B film formed, and the backing crystal dissolved. The resulting thin substrate and L-B film would be suitable for direct observation in TEM.

#### ACKNOWLEDGEMENT

This report was written under the auspices of the DARPA Materials Research Council, Contract #MDA903-83-C-0349 with The University of Michigan.

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## TOWARDS PERFECT OPTICAL COATINGS

A. Macleod, C. M. Stickley and E. Cross

### INTRODUCTION AND SUMMARY

With the announcement by President Reagan of a new DoD initiative to look for imaginative approaches to creating a defense against ballistic missiles armed with nuclear weapons came a re-examination in DARPA of possible thrusts which might satisfy his objectives given favorable development of the technology. Since ground or space based lasers (SBL's) is one such approach, it is prudent to examine the key limitations of lasers which might be removed if a serious research program were to be initiated. One of the most significant is clearly the premature failure, by at least a factor of three to five in energy density, of optical coatings on the laser components subjected to high pulse energies. This is illustrated in Fig. 1 by the distribution of failure probability which extends to  $60 \text{ J/cm}^2$  for a  $2.7 \text{ }\mu\text{m}$ , one microsecond laser pulse.

A meeting was held at the Materials Research Council to determine if there were opportunities in coatings research which, if pursued, might solve the key problems. Forty-seven researchers from thirty-four organizations met to present eighteen papers devoted to addressing this problem. Specifically, the attendees were asked to focus on the following three questions and to provide their recommendations to the MRC participants on these subjects:

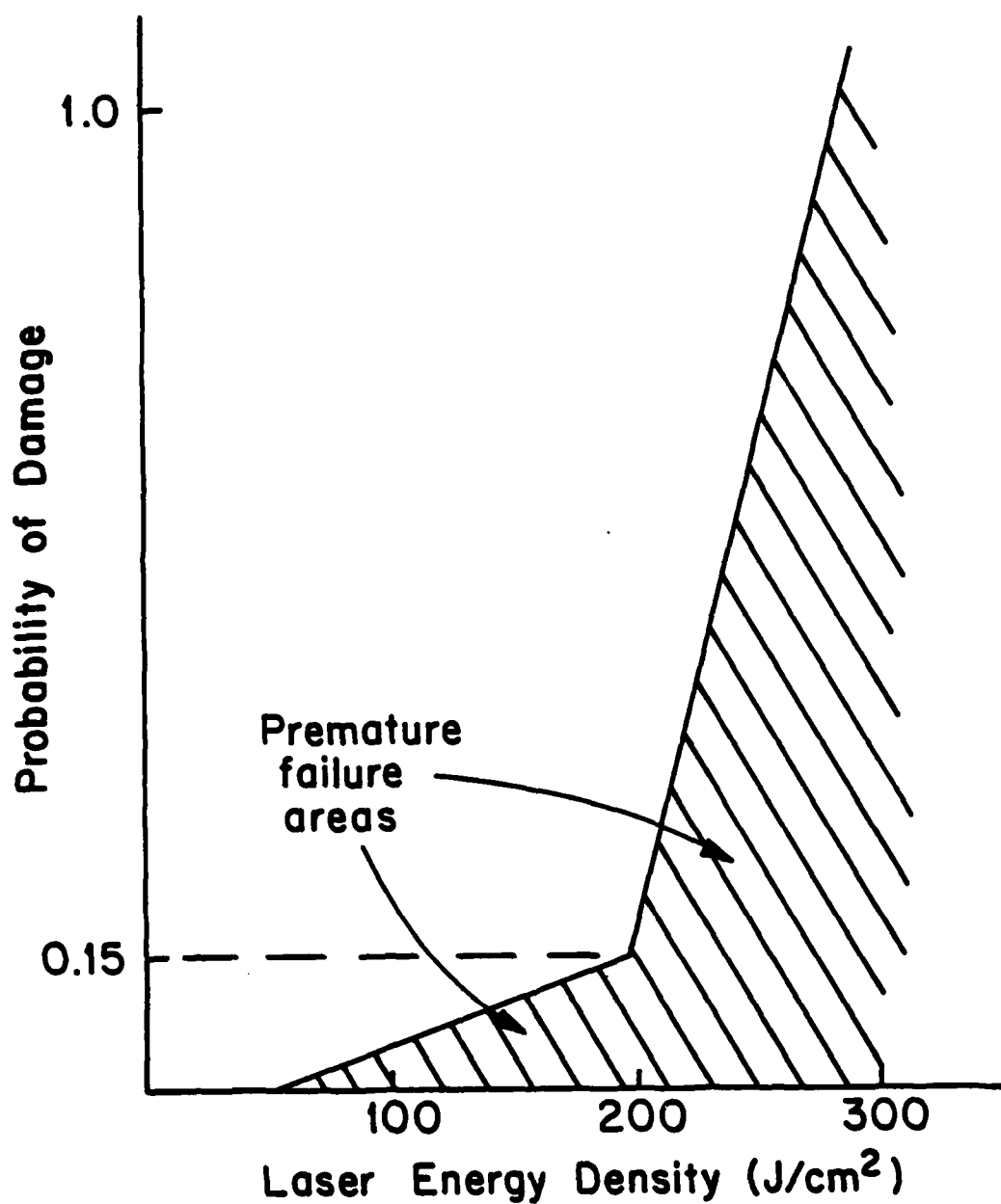


Figure 1. Probability of damage versus laser energy for a 2.7 micron HF laser with a nominal one microsecond pulse.



1. What is the relationship between coating microstructure and optical properties/coating performance? What is the ultimate performance and how "perfect" do coatings need to be to attain this performance?

2. What new techniques or refinements of techniques now in practice are capable of providing coatings of the required microstructure? What are the anticipated size/uniformity materials limitations of these?

3. Are quantitative relationships possible that relate deposition parameters and coating microstructure in analogy with phase diagrams?

While a variety of recommendations were made by the attendees, the overwhelming one was that a major, concentrated, dedicated effort should be initiated to systematically determine the reason(s) for premature coating breakdown in concert with the development of coating techniques and understanding which will lead to the solution of this problem. This recommendation is endorsed by the authors of this report based on the large payoff to the DoD if the research were to be successful, and on the fact that new coating techniques (magnetron RF sputtering, energy-assisted ion deposition, and others) appear to be at hand which might lead to understanding of this problem and to its eventual solution.

#### BACKGROUND

Laser induced damage in laser mirror coatings and other optical components came to be recognized as a limiting problem

for pulsed lasers as early as the mid-to-late 1960's. An early problem was damage in laser glass, and in 1970 the suggestion was made<sup>1,2</sup> that small platinum particles in the laser glass were responsible for premature damage. DARPA initiated a program to solve this problem in the glass laser and after several years of research it was successful.

During this period the MRC also investigated the more general problem of surface breakdown as it was seen on the ends of laser rods and in mirrors. Professor Bloembergen<sup>3</sup> made a key suggestion at that time which led to new approaches to surface polishing and which raised their breakdown level to nearly those observed to date (several joules/cm<sup>2</sup> for nanosecond duration pulses). Efforts since that time have been pursued primarily by the DoE laboratories and secondarily by the DoD and industry.

All of these efforts have been near-term oriented and have not had the necessary intensity over an extended period, with equipment and people devoted solely to this job, the dedication to solve the remaining but perhaps solvable problem, that of identifying and eliminating the submicroscopic defects at which premature coating breakdown is initiated.

It was with the hope of identifying approaches to this problem through developing satisfactory answers to the questions listed above, that this meeting was convened.

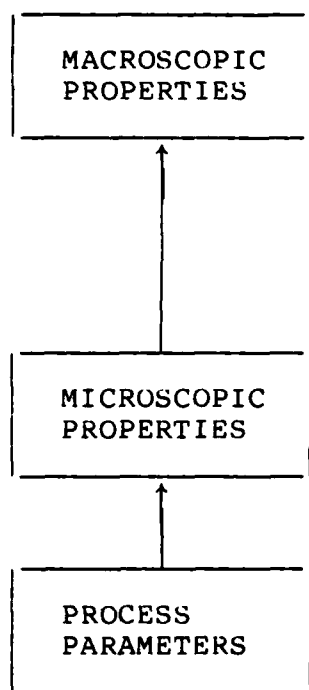
## ON THE RELATIONSHIP BETWEEN COATING MICROSTRUCTURE AND OPTICAL PROPERTIES/COATING PERFORMANCE

A major barrier to progress exists in our lack of understanding of the basic laser damage process. Although we can write a specification for a laser coating in terms of laser damage parameters such as threshold, we have no techniques for translating the specification into physical parameters such as grain size, impurity concentration, defect density, crystal structure and so on.

The plain fact is that we have no good idea of exactly what initiates laser damage in a particular coating. Damage initiates at sites which are not a priori detectable. They have been seen under certain conditions, however, to luminesce upon laser irradiation below the damage threshold. Following this lead may help us to develop a basic understanding of the origin of the defects causing premature coating breakdown. Without this basic understanding we are unable to adopt systematic fundamental methods in coating improvement to eliminate the low energy density "tail" shown in Fig. 1.

The key to not only the problem of laser damage but a wide range of other optical coating problems lies in the links between macroscopic and microscopic properties. These links are virtually unknown at present. Macroscopic properties are almost invariably those that we associate with coating performance and which we can usually measure, but processes for producing coatings operate, and must be understood at, the microscopic atomic and molecular level.

The various links are illustrated in Figure 2. Note the absence of a direct link between process parameters and macroscopic properties, which is assumed in the empirical approach. Without a detailed understanding of the influence of these microscopic coating features on overall performance we are forced to continue to seek still other empirical techniques; effective ones are difficult to find however since they have been sought for the past ten years.



NOTE:

There is no direct link between process parameters and macroscopic properties or performance. Yet empirical methods assume one.

Figure 2.

#### ON REFINEMENTS AND NEW TECHNIQUES FOR DEPOSITING COATINGS

The basic process for the deposition of optical coatings is still thermal evaporation in vacuo. This process has the great advantages of simplicity and flexibility in the wide range

of materials that can be deposited with almost no significant process changes required. Parametric variations in the films is, however, possible over limited regions only. Other processes are currently being investigated. New processes discussed at the meeting and which seem to hold great promise for new understanding and improvements in optical coatings, included ion-assisted deposition, magnetron RF sputtering, ion-beam sputtering, ionized cluster beam deposition, plasma polymerization, ion-beam deposition, molecular beam epitaxy, atomic layer epitaxy, and sol-gel processes. The sol-gel coatings show a greatly improved laser damage threshold when used as antireflection coatings. Little or nothing is known about the other processes in this context. The processes are all well-controlled so that consistent film parameters can be obtained and they appear to produce significant variations in the basic microstructural parameters from what is found in normally-evaporated films to make it of interest that laser-damage measurements should be performed. We do believe that assesment of the potential of these new processes for production of high laser damage threshold materials should be made.

#### ON QUANTITATIVE RELATIONSHIP BETWEEN DEPOSITION PARAMETERS AND COATING MICROSTRUCTURE

The measure of control of a process is determined by the extent to which the properties of this product respond systematically and consistently to deliberate variations in the control parameters. We can begin to understand the process only

when control is good enough so that we can plot the variation in properties in a multidimensional "phase diagram" with the process parameters as independent variables. The thin-film coating processes directly affect the microstructural properties of the layers, and it is essential for the success of the investigation we envisage that a high degree of control of layer microstructure should exist. It was clear from the meeting that considerable progress has been made in this direction. Thermal evaporation does not permit wide variation of layer microstructure. The major effects are produced by variations in substrate temperature (packing density and grain size increase with increasing temperature) and in background gas pressure when reactive evaporation is being performed. Considerable progress has clearly been made in sputtering. Data was described showing clearly the bounds of various crystalline and amorphous forms of  $\text{TiO}_2$  in terms of sputtering parameters. The excellent control possible in sputtering has been demonstrated in the construction of reflectors for the soft x-ray region. RMS surface roughness less than 1 Å has been achieved. The new ion-assisted processes, particularly those using this hot-cathode Kaufman sources with their very narrow range of ion energies, show exceptionally good control of microstructural properties such as packing density, crystallite size and crystal forms. These processes have the ability to control and reproduce materials in narrower regions of the microstructure phase diagram than ever before. They also appear to be able to achieve materials in

thin-film form which have density close to or equal to bulk values. To date, however, the characterization and understanding of the behavior of these films when exposed to laser radiation have not been undertaken.

#### CONCLUSIONS

The study of relationships between properties can only be as effective as the property measurements themselves. There are clearly great difficulties in the measurement of laser damage parameters such as threshold. Only a few facilities for such measurements exist where the characterization of the laser parameters is sufficiently precise to give the level of confidence required in results to be used in fundamental investigation. These facilities are required to produce immediate (3-6 months) results of importance to the construction and maintenance of specific laser systems so that they have little or no time for fundamental work.

Enormous amounts of data on laser-induced film damage exist but much of it is of little use for research purposes because of the lack of essential characterization of the films and differences in laser characteristics. Great difficulties are created by the almost infinite range of lasers and types of outputs which are available. The diffuse nature of the variety of lasers used presents further major difficulties with testing facilities. We therefore suggest limiting the attack on this problem to the use of one reliable, well-understood, stable, commercially available laser, such as a high energy-per-pulse

Nd:YAG laser with second and third harmonic generators to cover 0.53 and 0.35 microns and a hydrogen Raman down converter to approach two microns. A commercially available laser would enable the construction of one or more well characterized sets of laser damage testing equipment dedicated to research. The selection of this laser would be done in the first phase of a program to attack these problems; the laser would be chosen with an energy density and spot size capability so as to adequately address system requirements.

The type of research that we envision in the laser damage area requires rapid turn around of samples for laser damage measurement and a close link between processing, measurement, and characterization. These laser damage testing instruments should be associated with a coating facility with dedicated equipment for characterizing films in terms of composition and microstructure, and for helping to establish the connection between film microstructure and coating performance. The organization(s) where this work is performed should have the flexibility to move quickly both in terms of acquiring new people and equipment. Aspects of coating performance other than pure laser damage should be included in the investigation.

#### RECOMMENDATION

(1) We recommend an intense, three to five year focused attack on the laser coating damage problem which would involve the use of a dedicated laser/diagnostic test instrument in conjunction with several dedicated coating deposition research



systems. The program should be aimed at the improvement of understanding of the influence of coating microstructure on laser damage and other macroscopic properties with the long term goal being to eliminate the defects causing premature, low energy density coating failure.

(2) Such an effort should be preceded by a design study for a reliable, commercially available, visible wavelength, single frequency, single pulse length damage testing instrument. The emphasis on the study should be on reliability, repeatability, and ease of characterization.

(3) A broad investigation of the potential of new processes especially ion-assisted ones for the production of damage-resistant coatings, should be undertaken as a part of this research program.

#### ACKNOWLEDGEMENT

This report was written under the auspices of the DARPA Materials Research Council, Contract #MDA903-83-C-0349 with The University of Michigan.

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3. N. Bloembergen, "The Role of Cracks, Pores and Absorbing Inclusions on Laser Induced Damage Threshold at Surfaces of Transparent Dielectrics," MRC Summer Conference, Preliminary Reports, Memoranda and Technical Notes, Report 005020, pp. 285-300, July 1972.

MATERIALS RESEARCH COUNCIL  
TOWARDS PERFECT OPTICAL COATINGS  
July 6-7, 1983

July 6

Introduction, E. Joseph Friebele, Naval Res. Lab., Wash., DC

Current Problems in Coatings, T. M. Donovan, J. Porteus  
and J. L. Stanford, Naval Weapons Center

Thin-film Characterization, R. Messier, Pennsylvania State  
University

Sol-gel Coatings, D. Partlow, Westinghouse Research and  
Development; H. Lowdermilk, Lawrence Livermore National  
Laboratory

Ionized Cluster Beam Deposition, A. Kirkpatrick, Eaton Ion  
Systems, Inc.

Atomic Layer Epitaxy, Markus Pessa, Tampere University of  
Technology, Finland

Molecular Beam Epitaxy, M. Rona, Arthur D. Little, Inc.

Amorphous Optical Coatings and Sputtering, W. T. Pawlewicz,  
Battelle Pacific Northwest Laboratories

Some Topics in Sputter Deposition and X-ray Multilayers,  
T. Barbee, Stanford University

July 7

Ion-assisted Deposition of Optical Coatings, P. J. Martin,  
CSIRO Division of Applied Physics, Australia

Ion-Assisted Coating Deposition, R. McNeill, University of  
New Mexico

Some Aspects of Processing and Characterization of Oxide Films  
with Ion-assisted Reactive Evaporation, T. H. Allen, Optical  
Coating Laboratory, Inc.

Ion-beam Sputtering, J. Sites, Colorado State University

Amorphous Carbon Films and Ion-beam Deposition, T. J. Moravec,  
Honeywell Research Center

Unscheduled presentations

B. Newnam, Los Alamos National Laboratory

S. Pellicori, Santa Barbara Research Center

S. D. Jacobs, Laboratory for Laser Energetics,  
University of Rochester

A. K. Hopkins, Air Force Materials Laboratory

Discussion

ATTENDEES  
TOWARDS PERFECT OPTICAL COATINGS  
July 6, 1983

<u>Name</u>	<u>Affiliation</u>
H. A. Macleod	MRC/University of Arizona
C. M. Stickley	MRC/BDM Corporation
E. Joseph Friebele	DARPA-NRL
William Case	Vought Corporation
Robert Mehrabian	MRC/NBS
K. C. Jungling	Univ. of N. M.
J. K. McIver	Univ. of N. M.
P. J. Martin	CSIRO
I. J. Hodgkinson	University of Otago
James Sites	Colorado State Univ.
Marion Todd	Talandic Research Corp.
Bruce Steiner	Natl. Bureau of Standards
Cathy Peterson	Santa Barbara Research Cntr.
Samuel Pellicori	Santa Barbara Research Cntr.
John Neff	DARPA
J. L. Stanford	NWC China Lake
J. O. Porteus	NWC China Lake
Terry Donovan	NWC China Lake
Thomas J. Moravec	Honeywell
Joseph H. Apfel	OCLI
Russell Messier	Penn State University
Ursula Gibson	Univ. Of Arizona/OSC
W. Howard Lowdermilk	LLNL
Alan K. Hopkins	AF Materials Laboratory
Deborah Partlow	Westinghouse R & D Center
David Milam	LLNL
Markus Pessa	Tampere Univ. of Technology
Gary DeBell	Spectra Physics
Brian Newnam	Los Alamos Natl. Laboratory
Mehmet Rona	Arthur D. Little, Inc.
Bill Herrmann	Optic-Electronic Corp.
J. R. McNeil	University of New Mexico
T. H. Allen	OCLI
R. E. Klinger	OCLI
M. J.:. Soileau	North Texas State Univ.
Alan F. Stewart	AFWL/ARAO
Walter T. Pawlewicz	Battelle Northwest
Patricia Morse	AFWL/ARAO
Samuel Holmes	Northrop RTC
Frank Woodberry	Rockwell
S. D. Jacobs	University of Rochester
Ansgar Schmid	Washington State Univ.
Allen Kirkpatrick	Eaton Corporation
Frank W. Patten	DARPA
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Troy Barbee	Stanford University
B. Carnahan	University of Michigan

## UNCOOLED IR SENSORS

L. E. Cross and C. M. Stickley

### INTRODUCTION AND SUMMARY

Thermal imaging systems which could operate without the need for cooling would be a major step forward in the development of DOD equipment for use in the battlefield and in surveillance-type application. Such an achievement would eliminate coolers and the logistical problem and cost of coolant resupply, as well as lead to a thermal viewer which would eliminate scanning thereby becoming lighter in weight, lower in cost, and more reliable.

R. A. Reynolds of DARPA and L. E. Cross of the MRC organized a one-day meeting to examine uncooled infrared imaging technology to determine if materials and device research and development might make a significant difference in the outlook for developing such systems.

It was concluded that there are materials and device directions to pursue in hybrid local plane arrays using capacitive and pyroelectric ferroelectric sensing elements which, if successful, would have a noise equivalent thermal detective (NETD) of  $0.05^{\circ}$ - $0.1^{\circ}\text{C}$ . This report summarizes one meeting and delineates research direction which could lead to a 20 fold improvement in temperature sensitivity compared to that for pyroelectric vidicons.

## OUTLINE OF THE MEETING

Basic objectives for the meeting were:

1. To explore DOD needs and objectives for solid state uncooled imaging systems and to compare these with current plans and expectations for similar developments in the United Kingdom.

2. To examine systems and device structures currently planned or under development so as to highlight materials related problems amenable to pollution in these technologies.

3. To explore recent developments in ferroelectric single crystal, ceramic and composite structures which could be pertinent to present and emerging approaches to uncooled imagers.

The agenda for the meeting and the list of participants are attached in the appendix. In the first session, T. DePersia (NVEOL) outlined the DOD interest in Uncooled Infrared Imagers and the roles which these potentially simple inexpensive systems could fulfill. L. Garn (NVEOL) discussed some of the fundamental limits of uncooled thermal imagers emphasizing the critical importance of thermal isolation. R. Watton (RSRE) completed the first session by discussing British MOD expectations and objectives for both large linear and two dimensional thermal detector arrays.

B. Singer (N. American Philips) opened the second session with a discussion of the device and material considerations for the solid state pyroelectric imagers under development at Philips and Magnavox. He covered also the significant advantage

for the pyroelectric figure of merit of using ferroelectric single crystal cuts tilted with respect to the polar axis. N. Butler (Honeywell) described the gate coupled pyroelectric CCD devices at Honeywell. D. Cheung (Rockwell) discussed the pyroelectric material and device studies for imaging at the Rockwell Science Center. It was not possible, because of proprietary restriction, to have a full description of the dielectric imager developments at Texas Instruments, but K. McCormack gave a very brief account of some of the salient features of the T.I. system.

During the afternoon session, M. Liu (Honeywell) presented an overview of pyroelectric materials outlining the limited improvements which could be expected in single phase single crystal materials. A Bhalla (Penn State University) discussed pyroelectric composites and the critical role of the scale of heterogeneity in these systems. R. R. Neurgaonkar (Rockwell) underscored the advantages of the tungsten bronze family of ferroelectric crystals for pyroelectric device applications, and the important role of trivalent ion doping in these crystals. F. Ainger (Plessey, U.K.) described work upon high performance conducting pyroelectric ceramics in the modified lead zirconate family. In these materials a uranium doping can be used to control the resistivity providing the control resistor for a following FET stage.

## GENERAL SYSTEM CONSIDERATIONS

The elements of present hybrid thermal imaging systems are (Fig. 1): an image forming long wavelength IR lens, a radiation modulator, an array of thermal detectors at the focal plane, an electrical interconnect system to a silicon readout and signal processor which couples the detector outputs to a conventional CRT or similar readout device. Basically, the front end IR optics present an image of the thermal scene at the detector plane. The responsivity of the detector elements then depends on how the locally incident intensity is converted into temperature change and upon the transduction efficiency of the thermometric elements in converting this local  $\Delta T_e$  into a useful electrical signal, i.e.,

$$\text{Responsivity} = \Delta T_e \times \text{thermometric property}$$

For a given local incident flux  $I_0$  chopped sinusoidally at a frequency  $\omega$

$$\Delta T_e = \frac{I_0}{(g^2 + \omega^2 c^2 d^2)^{1/2}}$$

where  $I_0$  is the local absorbed intensity,  $g$  the thermal conductance from the element to its surroundings,  $c$  the volume thermal capacity and  $d$  the element thickness.

Clearly a large change of temperature  $\Delta T_e$  in the image plane, for a low  $\Delta T$  in the scene viewed, is always beneficial to array performance. To maximize  $\Delta T_e$  for a given chopping frequency  $\omega$ ,  $g$  must be kept small,  $c$  and  $d$  small, and  $I_0$  large.

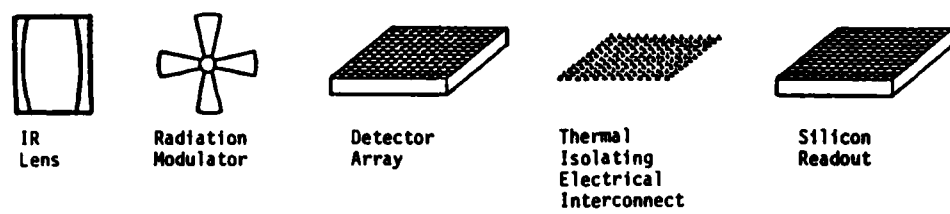


Figure 1. Schematic of essential components of a hybrid thermal imager.



In principle, the conversion efficiency of the thermometric material should also be high, but this must be consistent with low self noise. For transduction, it is natural to use materials properties already proven in thermal point detectors, and two phenomena both involving ferroelectric materials have been most extensively studied for this function,

(a) In the poled ferroelectric state, the pyroelectric property has been used to fabricate radiation detectors with near absolute theoretical sensitivity, detectivities  $D^* \approx 6 \cdot 10^9 \text{ cm} \sqrt{\text{Hz/W}}$  have been realized at room temperature.

(b) Alternatively in the paraelectric phase at temperatures just above the Curie-Weiss temperature, the very high rate of change of permittivity with temperature has been used in capacitance bolometers. Berman<sup>2</sup> reports values of  $D^* \approx 2 \cdot 10^9 \text{ cm} \sqrt{\text{Hz/W}}$  for  $(\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3$  ceramic elements at compositions  $x$  with Curie points close to but below room temperature.

Choice between these alternatives depends upon the multiplexing and coupling scheme in the electronics, and upon the mode of operation used.

Noise sources for all types of systems will include temperature noise, Johnson noise, and multiplexor and amplifier noise in the chosen readout scheme. For temperature noise in the detector element, the limiting detectivity  $D^*$  is given by

$$D^* = \frac{1}{\sqrt{4kT^2g}}$$

where  $k$  is Boltzmann's constant,  $T$  the absolute temperature of operation and  $g$  the thermal conduction to the surroundings. The importance of maintaining low thermal conductance to achieve acceptable detector noise performance is clearly evident.

For multiplexing and readout, CCD, JFET and MOSFET array structures have been used. Currently, the readout schemes do not appear to provide major limitations on performance and they were not a major topic of discussion at the meeting, except insofar as the specific scheme chosen reflects upon the requirements for the mating focal plane detector array.

#### CURRENT PERFORMANCE CAPABILITY

For systems discussed at the meeting: A modified lead zirconate  $16 \times 16$  element pyroelectric detector array with CCD readout, detector element area  $A_e \approx 256 \mu\text{m}^2$ , thickness  $30 \mu\text{m}$  and conductance  $g = 2 \text{ W/cm}^2\text{C}$  was shown to have a noise equivalent temperature at the detector (NETD) of  $0.5^\circ\text{C}$ .

In a  $32 \times 32$  element triglycine sulphate pyroelectric array with JFET readout, the NETD of  $0.6^\circ\text{C}$  was given. For the capacitive bolometer arrays with MOSFET switching precise figures of merit were not given, but the claim of a factor 4 improvement over current pyroelectric vidicons suggests an NETD of  $0.25^\circ\text{C}$ .

## PROBLEMS AND OPPORTUNITIES FOR FUTURE WORK

### SHORT RANGE

#### (1) Thermal Design

A substantial obstacle to improved performance is the thermal conductance to the detector elements inherent in most current commercial interconnect schemes ( $g \sim 1 \text{ watt/cm}^2 \text{ }^\circ\text{C}$ ). In research conditions,  $g$  values less than  $0.1 \text{ watt/cm}^2 \text{ }^\circ\text{C}$  have been realized and innovated interconnect schemes which can realize similar values in commercial practice are required to raise responsivity and relieve thermal noise limitations on detector performance. In thermal design it is probable that reticulation will become necessary as element sizes shrink and element thickness reaches the limits of practical bulk material processing.

Thinning techniques such as hydrophone polishing and ion milling may be borrowed from semiconductor microelectronics and element thicknesses down to  $10 \text{ } \mu\text{m}$  appear feasible. It is clear that current and projected short range requirements for dimensions are far from any limits which would begin to change bulk properties of the ferroelectrics currently in use for detectors.

#### (2) Ferroelectric Materials: Pyroelectrics

In the short term, triglycine sulphate (TGS) and strontium barium niobate (SBN) families appear to offer the best simple proper ferroelectrics for pyroelectric applications. Doping schemes (e.g. alanime doping for TED, and  $\text{La}^{3+}$  solid substitu-

tion for BSN) in these crystals give unexpected scope for improvement, and in both families tilted cuts can be used to further improve the figure of merit.

In both TGS and SBN families for 100  $\mu\text{m}$  square elements, 10  $\mu\text{m}$  thick, at a  $g$  value of  $0.1 \text{ W/cm}^2 \text{ }^\circ\text{C}$ , using CCD hybrid arrays, projected NETC  $\approx 0.05^\circ\text{C}$  at a field rate of 25 Hz, appears realizable.

### (3) Ferroelectric Materials: Capacitive Bolometers

For the capacitive bolometer arrays, the uncertainty is larger. Based on experience with capacitive point detectors it may be suggested that in ferroelectrics with a second order phase change at  $T_C$ , dielectric saturation will limit thermal sensitivity under high electric fields for temperatures close to the Curie point. Such limitations could possibly be relieved by moving to solid solution systems which exhibit a weak first order change at  $T_C$ . Unfortunately without knowing more detail of the operating conditions possible advances cannot be computed.

If AC interrogation can be used, high frequency operation will relieve Johnson noise limits, and resonant detector configurations can completely eliminate saturation effects.

### LONGER TERM

#### (1) Thermal Design

With increasing sophistication of the focal plane design, element size must shrink and the useful thermal receptor area will be reduced. It may then be valuable to explore radiation concentrators:

Less expensive alternatives to the F1 aperture lenses in current use.

Fly's eye lenses for concentration at the focal plane.

Antenna designs to couple radiation more effectively to smaller thermal elements.

## (2) Ferroelectric Materials

To effect more radical modifications of the thermal and electrical properties which constitute the 'figure of merit', 2 phase composite structures give a wider range of possibilities:

Systems such as Antimony Sulphur Iodide (SbSI) in a glass or plastic matrix phase have already demonstrated interesting bulk properties:

Processing techniques must, however, be devised to make composites on micron or sub-micron scales.

Tilted cuts exploiting both material and texture anisotropies in the composites could have interesting advantages.

Recent improvements in film deposition techniques for making highly ordered crystalline films upon low temperature substrates suggest that direct film deposition of ferroelectrics may be advantageous. With the submicron dimensions achievable capacitance limitations could enhance the utility of non-ferroelectric, pyroelectric, oriented crystal films. A 'high risk' extension to even thinner films of lower thermal mass could be the development of Langmuir-Blodgett films with polar pyroelectric character.

For dielectric bolometric applications, longer range developments will be dependent upon the formulation of rigorous figures of merit over the parameter ranges of operation in current and future devices.

### (3) Alternative Approaches

In the longer term some attention should be given to possible alternative techniques which are radically different from current hybrid approaches. Liquid crystal systems offer ferroelectric properties in conjunction with controllable optical character. Either alone or in conjunction with current pyroelectric charge generators, liquid crystals may permit direct optical readout of the thermal state of a detector array.

Resistive bolometers are competitive with capacitance and pyroelectrics as point detector elements. Theoretically both capacitive and resistive bolometers could be used without chopping if adequate matching of thermal properties could be achieved so as to avoid fixed pattern noise. It may be that in this respect resistive systems could permit more precise control.

### CONCLUSIONS

Current developments in hybrid focal plane arrays using capacitative and pyroelectric ferroelectric sensing elements have already demonstrated superior performance to the pyroelectric vidicon systems.

It would appear to be within foreseeable possibility if present technologies are vigorously pursued that NETD values less than  $0.1^{\circ}\text{C}$  can be achieved.

The simplicity, lower cost and logistic advantage of these uncooled systems may make up for lower sensitivity as compared to scanned photon detector systems.

#### ACKNOWLEDGEMENT

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PROGRAM FOR MATERIALS RESEARCH COUNCIL MEETING ON  
UNCOOLED THERMAL SENSORS

Friday, July 15, 1985

L. E. Cross (PSU)	Introductory
R. Reynolds (DARPA)	Remarks
T. DePersia (NVL)	DOD Interest in Uncooled Imagers
L. Garn (NVL)	Fundamental Limits of Uncooled Thermal Imagers
R. Watton (RSRE)	Ferroelectric Thermal Detectors Performance Aims for the 1980's
B. Singer (N. A. Phillips)	Device & Materials Considerations for Solid State Pyroelectric Imagers
N. Butler (Honeywell)	Gate Coupled Pyroelectric IR CCD's
D. Chung (Rockwell)	Pyroelectric Materials Applied to Devices: Figures of Merit & Beyond
M. Liu (Honeywell)	Overview of Pyroelectric Materials
W. Smith (N. A. Phillips)	Oblique Cuts in Pyroelectric Crystals
A. Bhalla (PSU)	Pyroelectric Composites
R. Neurgaonkar (Rockwell)	Applications of Pyroelectric Tungsten Bronze Materials for Thermal Detectors
F. Ainger (Plessey, UK)	High Performance Conducting Pyroelectric Ceramics
Discussion & Wrap-up	



ATTENDEE LIST  
UNCOOLED IR SENSORS

July 15, 1983

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K. McCormack	Texas Instruments	(214)995-2880
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SUMMARY OF THE WORKSHOP  
ON MICROSTRUCTURE AND TOUGHNESS

S. Fishman, J. P. Hirth, L. A. Jacobson and J. C. Williams

I. INTRODUCTION

At the 1982 MRC Summer Conference a workshop was held on the interrelation of microstructure and yield strength. In view of new possibilities for microstructure control in the rapid solidification technology area, the question arises concerning what constitutes the ideal or optimum microstructure for achieving the best properties. The aim of the 1982 workshop was to establish, if possible, guidelines for alloy design from the viewpoint of ideal microstructure to optimize yield strength. The objective was largely achieved as indicated in the Conference proceedings for 1982.

In 1983 a similar workshop was organized to examine the interrelation of microstructure and toughness. Contributions were made from the areas of ceramics, mechanics and metallurgy as indicated in the appended program. The first part of the following summary of the meeting is a set of Key Issues that emerged from the discussions. Next, in order, are summaries of presentations, summaries of discussions, and individual contributions.

## II. KEY ISSUES

### 1. Upper Shelf Toughness

In the higher temperature upper shelf regime in a plot of  $K_{IC}$  or  $J_{IC}$  vs. temperature for materials such as steels, the following factors were identified as being beneficial:

a. Strengthening particles should be well-bonded and adherent to decrease the likelihood of decohesion, thereby avoiding microvoid formation.

b. The particles should be small in size to decrease decohesion. The critical-size is an open issue, but it is definitely in the range of 100  $\mu\text{m}$  or less (see Evans, 1982 Report). In any case, a small size mitigates against multiple pileups which would greatly increase the local pileup stress (see Hirth, 1982 Report).

c. Particles should be as widely spaced as possible to avoid overlap of incompatibility stress fields. Thus, particle distributions should be as uniform as possible and there is a volume fraction limit of about 10% for avoidance of overlap effects. Also, as discussed by Hutchinson (see 1982 Report), for volume fractions greater than a critical value, failure ensues immediately after void nucleation. Thus, there is no point in attempting to modify void growth where the critical value is exceeded and the structure is not very defect tolerant under such conditions.

d. The thermal expansion coefficients of particle and matrix should be matched as closely as possible to avoid thermal

stresses. Particles should be rounded to avoid the stress irregularities associated with corners and should be as equiaxed as possible to avoid the multiple pileup effects mentioned in Item 1b.

e. Particle-matrix interfaces should have controlled solute or impurity adsorbates, avoiding damaging ones such as metal-loids in steel, but seeking additions which would enhance adhesion.

f. Particles should be semicoherent or incoherent to cause dislocations to bypass them rather than cutting them and to avoid coherency strains.

g. Inclusions should be avoided. If present and if weakly bonded to the interface, large, widely-spaced inclusions are less damaging than fine closely spaced inclusions, unless the latter are so very fine that they are smaller than the critical value in Item 1b.

h. Grain size should be fine to help minimize dislocation pileups. Experimental trends supporting this view have been found for both heat treated alloy steels and HSLA steels.

i. Grain boundaries should be free of large particles and should have controlled solute or impurity adsorbates as in Item 1e. The elements B, C, Mg and Zr have been found to be beneficial additions in such metals as iron and titanium.

j. Guidelines for elastic moduli are not simple. A matching of moduli of particle and matrix would reduce incompatibility stresses. On the other hand, relatively large modulus in

the particle would tend to "repel" dislocations and cracks, reducing stress concentrations at the interface and making decohesion less likely.

k. Guidelines for texture and grain shape are not simple. For uniaxial loading a selected texture or asymmetrical, aligned grain shape could decrease the tendency for cracking. Under situations where transverse or multiaxial loading were present, the beneficial effect would be less and indeed it could become detrimental.

l. Macroscopically, toughness can be enhanced by microstructures which promote a zigzag crack path (increasing the true fracture area per unit projected area) or crack branching. A well-documented example of the zigzag effect is in  $\alpha$ - $\beta$  titanium alloys where cracks tend to follow the interface of colonies of plates of Widmanstätten  $\alpha$ .

m. Factors that tend to increase slip planarity are unfavorable in that they promote dislocation pileup formation and, in turn, decohesion. These factors include low stacking fault energy (but see Item ln), fine coherent precipitates and solute effects. An example of the latter is the promotion of single  $\{110\}$  slip in iron by hydrogen. Coherent precipitates and solid solution hardening are desirable as secondary hardening effects together with fine dispersoids, however, as they then tend to raise yield and flow stress without decreasing the strain to failure markedly, thereby increasing toughness, see Item 3.

n. Final crack propagation and void linkup can occur in a mixed mode I-II manner as a consequence of plastic instability. The instability is manifested as a shear localization along the characteristic slip trajectories of continuum plasticity theory. Increased work hardening benefits toughness by decreasing the tendency for plastic instability. Therefore factors that increase work hardening are beneficial to toughness, including fine grain size, fine dispersed particles, and lower stacking fault energy (but see Item 1m).

## 2. Toughness in Al Alloys

As further discussed by Starke (Sect. V), some microstructural effects on toughness for precipitation hardened aluminum alloys are clearly defined. Toughness in these alloys is limited by microvoid formation and linkup as for the upper shelf case just discussed for steels. The trends are that toughness is enhanced by: decreasing or eliminating large dispersed particles of compounds of Al with Fe or Si, keeping hydrogen contents to 1 ppm or less, controlling texture to minimize anisotropy, avoiding recrystallization, maintaining fine grains, minimizing precipitate-free zones at boundaries (that would promote localized shear and fracture there), avoiding overaging which increases grain boundary precipitates and precipitate-free zones, and producing elongated grains. A new feature for these alloys is the role of PFZ's. Otherwise the trends are the same as those listed for Item 1 except for the grain shape effect. An opposite example for the latter effect

is the lower toughness of acicular ferrite compared to equiaxed ferrite in HSLA steels.

### 3. Constitutive Expressions for $J_{IC}$

The trends in toughness are consistent with a simplified expression for  $J_{IC} = \sigma_0 \epsilon_f l_0$ , where  $\sigma_0$  is the yield stress,  $l_0$  the spacing of microvoids ahead of the crack which establish the process zone of intense plastic deformation, and  $\epsilon_f$  is the fracture strain. Factors which decrease the likelihood of decohesion increase  $l_0$ . Factors which increase  $\sigma_0$  tend to decrease  $\epsilon_f$ , but this trend can be offset by such factors as grain boundary cleanliness. Also, when employed as secondary hardening mechanisms, precipitation or solid solution hardening tend to increase  $\sigma_0$  without influencing  $\epsilon_f$  as such. A somewhat more elaborate expressions for  $J_{IC}$  or for  $J$  as a function of stable crack growth is  $\delta a$ . However, these are two-dimensional in nature. Further work to develop more detailed constitutive equations, including three-dimensional microstructural effects and statistical variations in microstructural parameters is needed.

### 4. Interrelation among $J_{IC}$ , $T$ and $\sigma_0$ .

In the 1982 Report, the trend between  $J_{IC}$  and the tearing modulus  $T = (E/\sigma_0)^2 (dJ/da)$ , where  $E$  is Young's modulus, was unclear. An extensive compilations for steels cited by Rosenfield indicates now that  $J_{IC} \propto T$ , and such a trend has also been found in work by Cohen and his coworkers (see Sect. V). Moreover, it appears that experiments on similar types of materials fit a relation of the form  $J_{IC} \propto \sigma_0^{-2}$ . This, is

opposite to the direct interrelation presented in item 3 and indicates that  $\epsilon_f$  and  $l_0$  tend to decrease with increasing  $\sigma_0$ . More conventionally, since  $J_{IC} \propto K_{IC}^2$ , the above trend is equivalent to  $K_{IC} \propto \sigma_0^{-1}$ . Thus, to increase  $K_{IC}$  at a given  $\sigma_0$  one must move from one characteristic  $K_{IC}$ - $\sigma_0$  curve to another. As an example, maraging steels and NiCop steel lie on a curve of the above form, larger in  $K_{IC}$  at a given  $\sigma_0$  than that of conventional quenched and tempered steels. Both maraging steels and NiCop steels differ from conventional steels microstructurally in that they contain fine incoherent but adhesive precipitates.

#### 5. Shear Instability

The linking of large voids in uniaxial tension tests, the coalescence of a void and a growing crack tip and the onset of macroscopic cracking at blunt notches can occur by shear localization leading to failure by mixed mode I-II crack propagation. The latter two effects are pronounced under plane strain conditions. Ways to reduce the plastic instability are mentioned in item 1n. When limited by plastic instability, which generally initiates at a free surface, large inclusions do not have a marked role in crack propagation, microvoids forming at particles in the shear band path dominating the fracture process. An important issue requiring resolution is whether shear localization occurs first, creating void decohesion at particles by plastic incompatibility effects, or whether voids form first and promote shear localization. In either case the two effects mutually contribute to final fracture.



## 6. Transformation Toughening

Toughening by a phase transformation induced by near-crack-tip stresses has been successfully employed in partially stabilized zirconia. In principle, transformation can be used also for TRIP type steels. As discussed by Cohen (see Sect. V), the degree of toughening is quite sensitive to temperature, so the mechanism might be sensitive to exposure conditions. Hence, it should be applied with caution.

Also, as noted by Evans (Sect. V), when transformation toughening is employed, the crack tip moves into a transformed region. If the transformation product is less tough than the matrix, toughness will be degraded, tending to offset the beneficial effect of the transformation itself.

## 7. Lower Shelf Toughness

In the lower shelf region, cracking occurs by cleavage, sometimes with cleavage facets connected by plastically deforming ligaments. Rosenfield presented microstructural evidence for the Ritchie-Knott-Rice postulate that the critical event triggering cleavage is the formation of an unstable microcrack ahead of the main crack front, the microcrack growing to join the main crack. The microcrack growth involves the achievement of a critical stress at the site of a given critical flaw. The flaw is a cracked or decohered particle, supposed to be a grain boundary carbide in the R-K-R model. Rosenfield found MnS or grain boundary carbides as the crack origins. He also found that as  $T$  and hence  $K_{IC}$  increased, the spacing of the particle

from the boundary increased and the amount of stable crack growth prior to cleavage increased, supporting the R-K-R view qualitatively and indicating the importance of statistical variations in particle sizes and locations. With this background, the following factors influencing toughness were identified:

a. Evidence obtained by Cohen and others shows that microcracks extending from cracked particles often are arrested after traversing one grain. Thus, the critical flaw may in fact be either a cracked particle or a microcracked grain. It would be desirable to distinguish between these possibilities.

b. Factors controlling particle cracking and which would thereby enhance toughness are, for many of the same reasons discussed in item 1, fineness of particles, smooth particle shapes, equiaxial particle shapes, matched thermal expansion coefficients of particle and matrix, inherent ductility or at least fracture strength of the particle material, orientation of the particles such that their cleavage planes do not orient with those of the matrix in a manner to favor crack propagation (defeated by particle nucleation at grain boundaries), absence of coherency strains, and matching of particle-matrix elastic moduli to reduce incompatibility stresses.

c. Grain size should be as small as possible to limit the flaw size associated with microcracked grains and to limit pile-up stresses acting on particles.

d. Is the orientation change at a grain boundary, necessitating step formation or tearing ligaments for cleavage crack

propagation on a given  $\{hkl\}$  plane the factor leading to crack arrest at a grain boundary?

e. While there is evidence that the critical stress, or better, the critical stress intensity, to propagate a microcrack is constant at low temperatures, it may increase with temperature in the region of the ductile-brittle transition temperature. Further work on this topic is needed.

f. Further work on modeling of cleavage and the ductile brittle transition is desirable. It should include statistical considerations of the distribution of particles (size and position), extension of cracks from particles, and extension of microcracks across grain boundaries.

g. One would, of course, wish to avoid using a material in the temperature regime of the lower shelf. If it were necessary, however, the toughness could be improved by introducing large, decohered or weakly adherent particles into the material to act as crack arresters (see Drucker, Sect. V).

h. Grain boundary or particle interface solute or impurity adsorbates should be controlled as in the case of items 1e and 1i.

### III. SUMMARY OF PRESENTATIONS IN SESSION I

This session consisted of short invited presentations on a variety of topics related to microstructure and toughness. Fishman presented information on fracture behavior of metal matrix composites reinforced by hard particles or whiskers. While smooth bar fatigue data appears to compare favorably with that for aluminum alloys without reinforcement, crack growth rate ( $da/dn$  vs.  $\Delta K$ ) data are not encouraging, and notched fatigue behavior is quite unsatisfactory. Fracture toughness ( $K_{IC}$ ) values can be as low as half those of high strength aluminum alloys. However, composites which have oriented whiskers appear to exhibit substantial deflection of cracks propagating normal to the whisker direction. A question was posed as to possibilities for improving the toughness of particulate and whisker reinforced aluminum alloy composites.

Hucke discussed a number of microstructure variations in ceramic materials, with emphasis on SiC and carbon in which control of porosity leads to some interesting improvements in fracture behavior. Silicon carbide made by infiltrating porous carbon with molten silicon leads to residual tensile stresses due to the presence of free silicon which expands on solidifying, etching away or evaporating. This silicon gives a porous surface layer that responds to indentation toughness tests by crushing. This gives a material with a much higher apparent toughness.

Hutchinson discussed the brittle-ductile transition which occurs in plain carbon steels on increasing the test temperature. Toughness measurements in the transition region exhibit large scatter, and experiments for which microstructure variables have been introduced suggest that there is no simple connection between microstructure and toughness. A cleavage propagation mode dominates throughout the transition region, and it is suggested that the lowering of yield stress  $\sigma_0$  with increasing temperature may result in the stress in the plastic zone eventually becoming too low to initiate cleavage. A model based on the temperature variation of  $\sigma_0$  underestimates the increase in toughness through the transition zone. This suggests either that the critical stress for cleavage may increase with increasing temperature, or that the critical distance for microcrack linkup increases, or both.

Drucker reflected on some microstructure issues that were an outgrowth of efforts to develop materials with zero thermal expansion coefficient. Such materials have large volume fractions of hard particles in a ductile matrix, and fracture behavior/microstructure relations appear to be sensitive to the degree of bonding between the particles and the matrix. He proposed that unbonded particles lead to improved fracture resistance for larger particles, whereas for well bonded particles, larger interparticle spacing is beneficial.

Evans presented some new ideas regarding the role of microstructure variables in the transformation toughening of

ceramics. One can envision a process zone ahead of the crack, within which the transforming particles have been triggered. If the crack does not run through such a zone, no toughening effect would be expected. The wider this process zone, the greater the resistance to crack propagation, but the ways of increasing this width are not clear. There does appear to be an effect of the size of transforming particles, with maximum toughening contribution observed at intermediate sizes.

Observations on the cleavage fracture of steel in the ductile-brittle transition region were presented by Rosenfield.  $K_{IC}$  measurements in this region are complicated by the different micromechanisms. Origins of cleavage fractures appear to be MnS inclusions or grain boundary carbides that range up to 200  $\mu\text{m}$  ahead of the crack front. The scatter in toughness measurements is associated with the variability in the point where cleavage is triggered. There is a specimen size effect which is consistent with statistical fracture theory, in that large specimen toughness values lie at the lower end of the scatter band of measurements on small specimens.

Miller discussed the development of computer models for deformation and fracture under complex loadings and in diverse environments. Constitutive relations are used which take microstructure variables into account, and loading history is also considered in modeling local failure events.

Hirth reflected on some aspects of plastic instability in the fracture process. He questioned whether cracking in

metals is ever completely brittle, since shallow dimples are observed in intergranular and quasi-cleavage fracture. The effect of hydrogen on plastic instability as evidenced by increasing surface roughening on deformation may be linked to the promotion of (110) slip and the speeding up of screw dislocation motion, both of which lead to the formation of more concentrated slip bands.

Starke presented some observations on microstructure effects on fracture toughness in aluminum-lithium alloys. The coherent, shearable precipitates in these alloys can lead to planar slip and microcrack nucleation; precipitate free zones at grain boundaries can also lead to localized slip. Thermo-mechanical processing and compositional variations have been shown to ameliorate the tendency for slip localization, and raise the fracture toughness of these alloys to levels comparable to those of other high strength aluminum alloys. He also presented several guidelines for further increasing the toughness of Al-Li alloys.

Cohen presented some recent results on the toughening of steel by deformation-induced martensite. Two austenitic steels were tested, one of which was more stable than the other with respect to the formation of martensite. Tensile testing of the two steels shows martensite in only the less stable composition, whereas in fracture toughness tests, both steels exhibit deformation-induced martensite, probably due to the different stress state involved. Interpretation of these results is not

yet complete. However the doubling of toughness due to the transformation is more likely to be attributable to shear displacements than to the volume change.

Discussion of the relations among ductile fracture topography, ductility and toughness was contributed by Thompson, with emphasis on the modeling of microvoid coalescence. Changes in experimental conditions can be related to the volume fraction of particles which nucleate fracture, and to the fracture strain involved. Fracture surface microroughness, as determined by quantitative metallographic measurements, can be related to the fracture strain, and in combination with measured particle volume fractions and spacings lead to a potential relationship between microstructure and toughness. While this relationship remains to be tested, it may prove to be useful in assessing microstructural origins of fracture toughness.

Williams concluded the session by raising issues concerning the influence of the scale of microstructural effects on toughness. Crack deflection can be promoted by microstructural features of a size on the order of tens of micrometers, suggesting that the energy of deflection and the energy of propagation should be examined in order to gain some insight into the relative contributions of large scale and fine scale microstructural features. He suggested that such considerations may bring into question the hypothesis that fine grain size leads to higher toughness.



#### IV. SUMMARY OF DISCUSSION

The discussion centered on a list of topics which was drawn up by Hirth and Williams as an attempt to focus the discussion. This list is included as Table I. The bulk of the discussion was devoted to Item 1, The Role of Interfaces in Fracture, although Items 2, 3 and 6 also received limited attention.

The role of void nucleation and void growth were discussed by Hutchinson and by Thompson. One of the factors which seems unclear is the criterion for the lateral growth of voids. This is growth of voids so that their lateral dimension exceeds the original diameter of the nucleating particle. This point is relevant only in the case of small volume fractions of void nuclei where failure by void growth and coalescence occurs. In materials with high volume fractions of void nuclei, failure coincides with void nucleation and thus the lateral growth of voids is moot. At this time the issue of void growth and the onset of strain localization in connection with void formation and growth is largely unresolved. This point is of central importance to solving the question of toughness improvement because of the predominant tendency of high strength materials to exhibit strain localization.

In a related issue the applicability of the proportionality between  $J_{IC}$  and the product  $\sigma_0 \epsilon_f l_0$  was discussed. Here  $\sigma_0$  is the yield stress,  $\epsilon_f$  is the fracture strain and  $l_0$  is a characteristic length over which the fracture event occurs.

TABLE 1. SUGGESTED DISCUSSION TOPICS

1. Role of interfaces in fracture
  - a) Size dependence of second phase decohesion
  - b) Void nucleation vs. void growth
  - c) What type of interface (strengthwise)  
for: strength, toughness, fatigue
2. Role of cleavage cracks in fracture
  - a)  $\sigma_0$  not constant with varying T
  - b) Is K vs. RA only/mainly a statistic problem
  - c) Role of microcracks ahead of main crack front
3. Transformation toughening
  - a) Multiple "strength" sites useful
  - b) Effect of load vs. displacement control
4. Crack Path Effects
  - a) Tortuosity
  - b) Interaction with voids
5. Role of plastic instability on fracture
6. Relationship between T and J
7. Role of continuum effects in fracture
  - a) Specimen size
  - b) Mixed mode cracks
  - c) Blunting line in J vs.  $\Delta a$  curve

This relation seems to hold for many materials, however it was agreed that a better understanding of the relationship between  $\lambda_0$  and microstructure was required. Such a relationship could also guide microstructural tailoring (design) to provide improved toughness. Further experimental and analytical work on this point appears warranted. In connection with the usefulness of the  $J_{IC} \approx \sigma_0 \epsilon_f \lambda_0$  relation, Cohen asked if the "wavelength" of crack tortuosity was related to  $\lambda_0$ . Here again there was no clear consensus but this question is also important in relating  $\lambda_0$  to microstructure. Williams suggested that there may be two or more relevant  $\lambda_0$  values in complex microstructures. This is where crack tortuosity is superimposed on local ductile fracture. There may be characteristic lengths which control the contribution of each to the fracture mode and energy.

Rosenfield also offered some comments on measuring toughness. Using ASTM A508 steel as an example, he suggested that when  $K/\sigma_0 > 3\sqrt{in}$ , measurement of  $K_{IC}$  becomes virtually impossible. He also suggested some guidelines for improving the toughness of steel. These include minimizing cleavage by reducing inclusion content, removing grain boundary precipitates, refining grain size and controlling texture to reduce the the normal stress across  $\{001\}$ . He mentioned that maraging steel and an HSLA steel (NiCop) achieved  $K/\sigma_0 \approx 2\sqrt{in}$ , almost at the "completely tough" limit mentioned above.

There also was extensive discussion of the role of particle size and particle/matrix interface strength in ductile

fracture. The idea that a minimum size exists below which decohesion does not occur seemed to be generally accepted. However, the limiting size or size cut off for particles to act as void nuclei seems to be less clear. Several factors seem to pertain: e.g., the strength of the interface bond and the particle shape. The Edelson-Baldwin hyperbolic relation between fracture strain and particle volume fraction seems to flatten out with increasing interface strength. The cases of MnS vs Fe<sub>3</sub>C in steel seem to support this. The more ready decohesion of interfaces of plates vs. spheres seems also to be borne out by plates vs. spheres of Fe<sub>3</sub>C in steel. Evans suggested that stress concentrations at corners were responsible for this effect.

Cooper suggested that the shape of the ductile-brittle transition curves in steels were similar to the temperature derivative of viscosity plotted against temperature for polymers. The lower shelf of each curve is characterized by limited flow (long relaxation times). Beyond that the relation between physical processes in the two cases becomes less clear.

Ritchie contributed a prepared discussion on fatigue crack growth using crack closure during unloading and reloading as the focus for his remarks. He commented that closure of the crack is most commonly caused by oxide formation in the crack tip region or by crack surface roughness. Closure allows the crack to be partially wedged or propped open during unloading. As a result a portion of the applied cyclic stress intensity is expended in re-opening the crack tip with attendant reduction in

the driving force available to extend the crack. Ritchie divides metallurgical factors which affect crack growth rate as intrinsic and extrinsic where closure is included in the latter. A critical test for existence of an intrinsic factor is to conduct fatigue crack growth rate experiments under conditions where closure does not occur. One example would be high load ratio (R) tests. Another is propagation of short cracks where there is no crack "wake" to close. In fact both of these types of experiments remove the effect of microstructure on crack growth rate when the microstructural effects are manifested as closure. Ritchie emphasized the need for identifying intrinsic microstructure effects on crack growth since these effects will lead to more universal improvement in crack growth characteristics.

Hutchinson pointed out that the transition region in a  $K_{IC}$ -T plot was not clearly understood. The Ritchie-Knott-Rice theory, which fits the lower shelf region well, exhibits a much smaller increase with T than actual data. A possible cause is that the critical cleavage stress, instead of being constant, increases in the DBTT region.

V-1. THE RELATIONS AMONG DUCTILE FRACTURE TOPOGRAPHY,  
DUCTILITY AND TOUGHNESS

Anthony W. Thompson

When ductile fracture (microvoid coalescence or MVC) is controlled by nucleation at second-phase particles, as it usually is when the particle-matrix bond is not strong, the process is readily modeled in terms of the volume fraction,  $f$ , of particles which in fact nucleate fracture. Particularly when one compares two experimental conditions (changing temperature, strain rate, hydrogen content, or other variables) which both result in complete MVC, it is convenient to write (for a change "x" in conditions),

$$\frac{\epsilon_f}{\epsilon_f^x} = \frac{f^x}{f} \quad (1)$$

where  $\epsilon_f$  is fracture strain. Quantitative metallographic relations then readily give, for dimple diameters  $D$ ,

$$D^x/D \cong C_1 \sqrt{\epsilon_f^x/\epsilon_f} \quad (2)$$

where  $C_1$  is a constant depending on the fracture surface micro-roughness  $M$  as  $(1-M)$ ;  $M$  is defined as

$$M \equiv h/w \quad (3)$$

for  $h$  = depth and  $w$  = width or diameter of dimples. For particle diameters  $d$ , it can be shown that

$$h/d \approx (M^2/3f)^{1/3}$$

and since  $h/d$  is a measure of the local strain at the particle,

$$\epsilon_f \approx \ln(h/d) = \frac{1}{3} \ln(M^2/3f) \quad (4)$$

When toughness is written as a product  $\sigma_o \cdot \epsilon_f \cdot L$ , with  $\sigma_o$  a (work hardened) flow stress and  $L$  a microstructural length, then

$$J_{IC} \approx \frac{\sigma_o L}{3} \ln\left(\frac{M^2}{3f}\right) \quad (5)$$

This has the advantage that  $\epsilon_f$ , a difficult quantity to measure with confidence under crack-tip conditions, is replaced by a term involving the more readily measured  $M$  and  $f$ .

Equation (3) has been shown to describe a number of reported  $D^X/D$  values. Equation (5) remains to be tested, but may be useful in assessing microstructural origins of fracture toughness.

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V-2. CLEAVAGE FRACTURE OF STEEL IN THE DUCTILE-BRITTLE  
TRANSITION REGION

A. R. Rosenfield

Measurement of  $K_{IC}$  in the ductile/brittle transition region of steel is complicated by the differing nature of the two micromechanisms involved. We have found that the origins of cleavage fractures of ASTM A508 steel are MnS inclusions or grain boundary carbides lying up to 200  $\mu\text{m}$  ahead of the main crack front. These results, and some earlier ones, suggest that cleavage fracture requires the formation of microcracks at special sites and their subsequent propagation. The activation strengths of these sites appear to have a broad distribution, and they appear to be scattered through the microstructure. In accord with statistical fracture theory, the toughness of large specimens lies at the lower end of the range of toughnesses of small specimens. Detailed fractographic studies combined with factoring-out complications associated with the intervention of dimpled rupture can aid in overcoming the problem of predicting large-specimen behavior from small-specimen data.

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E. A. Starke

In a DARPA supported program, Lockheed Missile and Space Center showed that the materials property improvement that will give the largest reduction in weight of present and future aircraft is a reduction in density. Lithium is the lightest metal and has the most potent effect on both density and elastic modulus of all possible alloying additions to Al. It has been used previously in a commercial Al alloy, X2020, and was successful in reducing density, increasing modulus and strength when compared to other available high strength Al alloys. However, its low ductility and fracture toughness resulted in its removal from the market in the early 1960's.

The low fracture toughness was initially attributed to Na, a normal impurity in Li, segregating to grain boundaries and enhancing intergranular fracture, or to high levels of hydrogen which were believed to be present in the highly reactive Li containing alloys. Work at Alcoa showed that high levels of Na do not embrittle AL-Li alloys in the age hardened condition. Other recent research has shown that the amount of hydrogen necessary to cause embrittlement far exceeds that detected in X2020 or Al-Li alloys prepared by current melting and casting methods. Sanders and Starke clearly showed that the low ductility was due to strain localization resulting from local loss of strength during shearing by mobile dislocations of the coherent

strengthening precipitates and the presence of PFZ's in the peak strength temper. Subsequently, Lin and Starke showed that an excellent combination of strength and ductility could be obtained by special thermal-mechanical processing which resulted in a sharp texture and an unrecrystallized structure which minimized the effect of PFZ's. However, no improvement in fracture toughness was obtained because of the presence of large Fe and Si constituent phases. A significant improvement was obtained after removing the constituent phases and replacing Mn with Zr which changed the type of dispersoid from large ( $\sim 2\mu\text{m}$ ) incoherent dispersoids to smaller ( $\sim 200\text{\AA}$ ) coherent dispersoids.

These practices were not sufficient to improve the fracture toughness in Al-Li- $\alpha$  alloys when Li content was equal to or exceeded 2 wt % because of the presence of PFZ's at both high angle and low angle subgrain boundaries. Alloying additions, e.g. Cu, Mg, and TMT's were used in combination in a DARPA supported program at Lockheed Missile and Space Center to essentially eliminate the PFZ's and homogenize deformation during mechanical working. Fracture toughness values of these new alloys approach those of other high strength Al alloys and their commercial utilization appears to be imminent. The Al-Li alloy development program, along with other research on Al alloys has shown that the following guidelines may increase toughness of Al-Li alloys:

1. Minimize the volume fraction of insoluble constituents by increasing base purity.

2. Keep hydrogen levels below 1 ppm.
3. Control texture to minimize anisotropy.
4. Adjust processing practices to promote the lowest degree of recrystallization.
5. In recrystallized structures, e.g. sheet material, keep grain size to a minimum and use practices that produce elongated grains.
6. Try to keep PFZ's to a minimum by TMT's and composition control.
7. Decrease the number of dispersoids by adjustments in chemistry and TMT.
8. Underaged and peak aged structures are normally better than overaged structures since they have less grain boundary precipitates and PFZ's.

E. A. Starke

Following are some comments on the relation for  $J_{IC}$ ,  $J_{IC} \cong \sigma_0 \epsilon_f l_0$ , where  $\sigma_0$  is yield strength,  $\epsilon_f$  is fracture strain and  $l_0$  is process zone size.

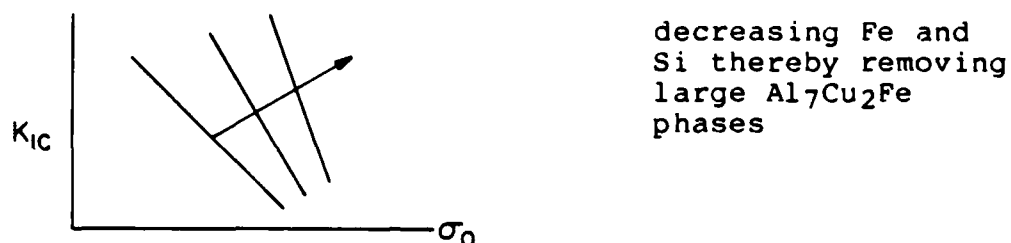
## ROLE OF INTERFACES IN FRACTURE

a) Size dependence of second phase decohesion - experimental observations clearly show that large particles,  $>2\mu\text{m}$  are much more detrimental than smaller ones  $<1\mu\text{m}$ . The relationship between the size and nucleation may be associated with the more irregular shape of large particles resulting in stress concentrations at corners, etc. which aid decohesion. This effect is enhanced when large differences exist between the modulus of the matrix and the particle. Other effects may be associated with the probability of slip band intersection, fracture during processing, etc.

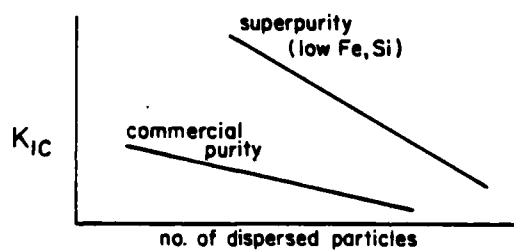
b) Properties of particles, e.g. modulus, coefficient of thermal expansion -modulus effects can increase stress concentrations at ends of irregular shaped particles, and large differences in coefficient of thermal expansion may result in residual stresses during cooling from high temperatures that may subsequently aid decohesion.

It appears that particle size, shape and properties could be included in the fracture toughness models in the  $\epsilon_f$  parameter. The  $l_0$  parameter is probably related to void growth

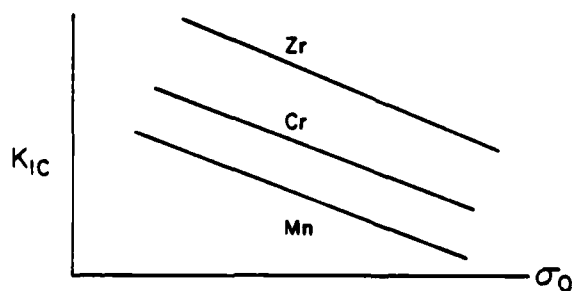
and may be associated with particle spacing. In Al alloys significant improvement in  $K_{IC}$  occurs when large constituents are removed, Fig. 1:



However, further improvement is obtained when the number density of dispersoids is lowered,



probably by decreasing the probability of void sheets forming between constituent phases. The type of dispersion also has an effect.



At present, no theoretical analyses of these observations have been attempted in Al alloys.

J. P. Hirth

Plastic instability influences fracture in a number of ways, some not completely understood. One may ask the question whether fracture is ever completely brittle. S. Lynch has studied both intergranular and cleavage-type fracture surfaces of specimens degraded by stress-corrosion cracking, hydrogen embrittlement or liquid metal embrittlement. While the surfaces appear flat in SEM, they show shallow dimples when observed at high resolution using replica TEM. Also, as shown long ago by I. M. Bernstein, single crystals of iron fail at very low temperatures with little elongation in a mixed mode I-II fracture that follows a  $\{110\}$  slip trace. Hence, these failures may be triggered by a shear instability. In a general sense, the yield strength increases as temperature  $T$  decreases while the tensile strength remains relatively unchanged. This means that the work hardening rate  $d\sigma/d\epsilon$  decreases as  $T$  decreases, indeed, as observed experimentally, which would favor the onset of shear instability, particularly under plane strain conditions.

Our observations of the critical strain for the initiation of surface roughening in plane strain tensile or bend testing of spheriodized 1090 steel gives results ( $\epsilon^*=0.27$ ) in very good agreement with the recent theory of Hutchinson that Tvergaard ( $\epsilon^*=0.24$ ). The surface roughness is a manifestation of plastic instability and eventually leads to the generation of

shear instabilities. The theory is based on a yield surface with a corner, and one may ask what is the basis for a corner. One possibility would be geometric softening in the sense of a slip system rotating in such a way that the resolved shear stress on it increased. This type of model fits evidence for single crystals (Asaro, Needleman) but no evidence is available for polycrystals where multiple slip occurs. The presence of defects (voids, microcracks) also could induce a corner.

Of interest in correlation with theory as well as in connection with mechanisms, shear instabilities occur at much lower strains ( $\epsilon^* \approx 0.13$ ) in hydrogen charged specimens even though  $\sigma_0$  and  $d\sigma/d\epsilon$  are unchanged so that theory would still predict  $\epsilon^* = 24$ . A possible explanation is connected to other results of Hutchinson and Tvergaard. They found that the imposition of an initial sinusoidal surface roughness decreased the critical strain  $\epsilon^*$  at which the roughness amplitude increases dramatically by about 33%. Theoretical interpretations of stress-strain curves and internal friction, and recent in-situ deformation studies by TEM (Birnbaum) show that hydrogen in iron both softens the iron by making screw dislocation motion by a double-kink mechanism easier and enhances planarity of slip on  $\{110\}$  planes. So one can then imagine, in hydrogen charged iron, a set of intense slip bands at the surface extending over about a grain diameter. The slip bands are tantamount to small mixed mode I-II cracks and are thus the mixed-mode analogs of the sinusoidal roughness. Hence, the theoretical  $\epsilon^*$  could be

lowered and agreement between theory and experiment restored. The implication for the mechanism of hydrogen embrittlement is that hydrogen degrades materials suffering ductile fracture by enhancing the onset of shear instability.

Shear localization can lead to failure by connecting large voids in uniaxial tension specimens, by connecting a blunt crack tip to a void ahead of it, or by initiating a crack at a blunt notch. An important issue is unresolved with regard to the mechanism of the initiation of shear localization. Once shear has localized, particles in the sheared region generate large incompatibility stresses leading to decohesion of the particle interfaces and void formation. If voids form, they enhance shear localization. Thus, voids and shearing interact and lead to eventual mixed mode I-II cracking. The open question is whether void formation or shearing initiates first. In the hydrogen embrittlement case discussed above, the shearing appears to begin first but this may not be general.

At the crystal plasticity level, the situation is fairly clear. Planar slip is promoted by low stacking fault energy, a limited number of slip systems and by special solute interactions such as the case mentioned of hydrogen in iron. Slip band, shear instability occurs in coherent precipitate systems where the particles are cut; in irradiation hardened systems where debris is swept up by dislocations; and when dislocations break away from solute atmospheres.



At the dislocation level, dynamic pileup inertia effects may be important. Steady state motion solutions show that dislocations have a substantial effective mass that increases in a relativistic manner at both the sound velocity and the Rayleigh velocity. Eshelby obtained a mode III, approximate crack solution that indicated no inertia for an accelerating crack, which seems inconsistent with the constant velocity result. Atomic simulations indicate that cracks do have inertia, contrary to the Eshelby result. Thus, dynamic effects can be important in transmitting dislocations or shear bands across grain boundaries or other obstacles, a contributing factor in shear instability. Theoretical work is required to resolve the Eshelby quandary.

A NOTE ON MICROSTRUCTURAL DESIGN  
FOR STRENGTH AND TOUGHNESS

D. C. Drucker

Two extreme approaches to strength and fracture toughness are presented. One aims at perfection of the microstructure and achieving the very highest level of strength and toughness possible. The other aims at no more than adequate strength and toughness for the application in mind. Large inclusions that serve as holes are introduced purposefully to reduce triaxiality and tensile stress level, to set the scale of the region deforming plastically during separation, and so increase the microscopic ductility of the matrix in front of the crack and guarantee a modest but acceptable toughness.

The design of the microstructure of a metallic alloy for flow strength and toughness can be approached in many ways. One, of great appeal and appropriateness when both very high strength and high toughness are required, is to aim at the strongest possible microstructure free of defects that limit the overall plastic strain and prevent development of the fully plastic response mode. Standard and special strengthening techniques are employed using fine dispersions and precipitates, or more generally fine subgrain structure. With this approach, dispersoids must be so strongly bonded to the matrix that voids are not initiated at the interfaces when the material is highly deformed plastically at high stress levels in the vicinity of

the root of a crack or a notch. Grain boundary sources of voids or cracks similarly must be eliminated along with large inclusions. All brittle constituents should be isolated from each other by a highly ductile matrix.

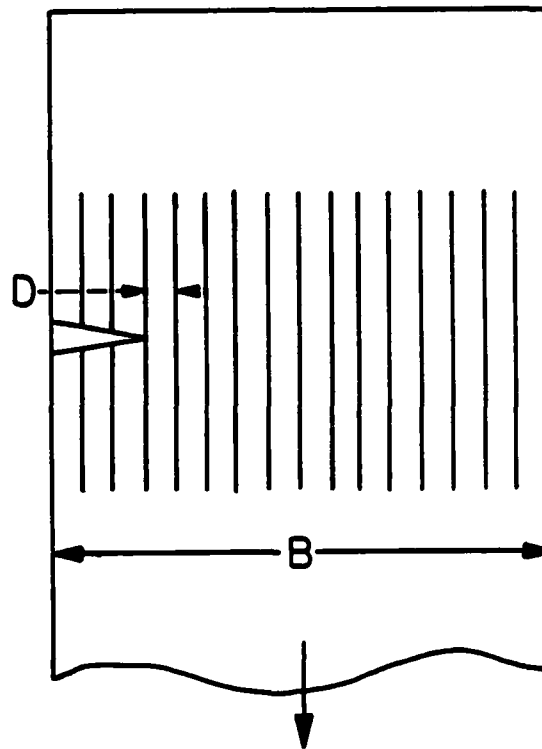
To the extent that all these good things and more can be achieved, the material will be very strong and will be very ductile on the small microscale (micrometer and submicrometer dimensions). If no microstructural defects at all exist or develop during plastic deformation, gross plastic strains are not limited by the microstructure. The region that deforms plastically after maximum load is reached and before, is of the largest possible volume for the given geometry of the body and the loading. Consequently toughness as well as load is just about as great as possible for the flow strength of the material.

Sharp cracks will blunt and plastic limit loads will be reached prior to the fully plastic pattern of separation on the macroscale. Overall shape and dimensions of the body or test specimen govern. In this perfect material there is no microstructural scale that enters into the geometry of the deformation to failure.

An alternative approach has a much less ambitious goal. It assumes that defects in large number are all too likely to be present on a variety of microscales from submicrometers to hundreds of micrometers, that debonding of small as well as large precipitates, dispersoids, and other inclusions is likely to occur in front of a sharp crack as a result of the surrounding

plastic deformation and high stress. Low macroscopic local ductility, and low fracture toughness, then will result from the initiation and growth of voids in void sheets under tension or combined tension and shear, no matter how ductile the matrix.

If the body were under uniaxial tension, a set of parallel bars joined at their ends (instead of a continuous body) would minimize or delay the void initiation and coalescence by eliminating the triaxial stress ahead of the crack and substantially reducing the tensile stress remaining to initiate and grow holes.



After the maximum load is reached in the bar, the local stretching prior to separation is of the order of the bar width  $D$ . The fracture toughness or  $K_C$  value that results is of course far smaller than for the perfect material in which the plastic separation beyond maximum load is of order  $B$ , the total width. However, if

$$G \cong 1/2 \sigma_0 D \quad (1)$$

$$K_C \cong \sqrt{1/2 \sigma_0 E D} \quad (2)$$

where  $\sigma_0$  is the flow strength in simple tension and  $E$  is Young's modulus, is adequate toughness for the purpose at hand it may be better to play safe and not aim for greater perfection.

Of course, the assemblage of independent bars is a one-dimensional material with zero transverse strength. A three-dimensional material with somewhat similar attributes for all directions of loading can be achieved with a uniformly dispersed array of weakly bonded ceramic particles of diameter  $d$  and spacing  $D$ , provided  $d/D$  is large enough. At working stress levels the interface between particles and metallic matrix is likely to be under compression due to differential thermal contraction on cooling down from the temperature of manufacture. Therefore the thermal and the elastic properties are likely to be about those for a fully bonded interface. However, any ordinary bond will break in the region in front of a stationary or advancing crack to produce the equivalent of holes of diameter  $d$  in the ductile

matrix. With a sufficient volume fraction of weakly bonded particles the stress level in the matrix can be kept below the void initiation and growth threshold stress for the very small sub-micrometer particles that strengthen the ductile matrix, at least until large plastic strains occur in the matrix during the process of ductile separation.

The selection of  $d$  and  $D$  to guarantee an adequate toughness

$$K_C \approx \sqrt{1/2 \sigma_0 E D} \quad (4)$$

does involve some sacrifice of effective flow stress  $\sigma_0$  due to the holes and abandoning the hope of creating a more perfect material with a larger effective  $D$ . The higher the dependable bond strength between the submicron particles and the matrix they strengthen, the larger the  $D$  of the large inclusions can be.

V-7.

MICROCRACK FORMATION IN IRON BY CRACKING  
OF GRAIN-BOUNDARY CARBIDES

A Statistical Treatment

Morris Cohen

During the workshop, there was some discussion concerning the formation of microcracks in ferritic grains and their abundance as a function of test temperature and metallurgical variables. A detailed paper on this subject has been published by M. Cohen and M. R. Vukceovich in Physics of Strength and Plasticity, A. S. Argon, ed., MIT Press, 1969, pp. 295-305. The essential findings relevant to the current interests are as follows:

1. Grain-boundary carbides in iron-carbon alloys and mild steels are subject to cracking during tensile testing, and thereby produce internal flaws for potential cleavage of the adjacent ferritic grains. The extent of carbide cracking increases with plastic straining of the specimen, and the form of the crack length distribution depends on the thickness of the grain-boundary carbides that are present.

2. The number of ferrite microcleavages initiated at each point along the stress-strain curve can be calculated graphically, based on the number of carbide cracks that are supercritical in length (according to some fracture criterion, such as that of Griffith-Orowan) when they came into existence. Carbide cracks which do not happen to satisfy this condition at

the time of their formation become blunted, and are taken to remain inert relative to microcleavage of the ferrite throughout the further stressing.

3. These considerations permit calculation of the number of microcleavages observed in tensile specimens tested at various temperatures ranging from below to above the ductility-transition temperature. Bell-shaped curves are obtained, with maxima coming at temperatures somewhat below the ductility transition.

4. The effects of carbon content and ferritic grain size on the temperature dependence of the numbers of microcracks can also be calculated under the foregoing assumptions, inasmuch as the thickness of the grain-boundary carbides varies in a systematic way with carbon content and grain size.



V-8. FRACTURE TOUGHENING OF STEEL BY DEFORMATION-INDUCED  
MARTENSITIC TRANSFORMATION

Morris Cohen

Two austenitic steels with yield strengths of about 1.2 GPa (175 ksi) at room temperature have been prepared with different degrees of metastability relative to deformation-induced martensitic transformation. Both steels contain 31 w/oNi and various other alloying elements to help bring the yield strength level up to 1.2 GPa which is quite high for austenitic steels. Chromium was added to one of steels to make the austensite more stable than the base composition, thus providing a basis of comparison for showing the effect of transformation toughening in  $J_{IC}$  tests as a function of temperature.

The  $J_{IC}$  vs. temperature curves of both steels exhibit three regimes:

Regime I. This is the highest temperature regime studied.

$J_{IC}$  decreases with decreasing temperature to a minimum. The austenite does not undergo deformation-induced transformation over this range of temperatures. The reason for the decrease in  $J_{IC}$  is not clear at the present time. The fracture is of the zigzag type, and this seems to become more pronounced with decreasing test temperature.

Regime II. In this intermediate-temperature regime, the austenite undergoes deformation-induced transformation at the advancing crack tip, and the extent of transformation increases with decreasing test temperature. Concomitantly,  $J_{IC}$  increases with decreasing temperature and reaches a maximum.

Regime III. This is the lowest temperature regime. Here,  $J_{IC}$  decrease with decreasing temperature, while the amount of deformation-induced transformation increases extensively.

Some key data are given below:

	Base Composition		Base Composition +5 w/o Cr	
	Temp.°C	$J_{IC}, \text{kJ/m}^2$ (in.-lb./in. <sup>2</sup> )	Temp.°C	$J_{IC}, \text{kJ/m}^2$ (in.-lb./in. <sup>2</sup> )
Minimum $J_{IC}$ (Between Regimes I & II)	175	104 (600)	100	112 (650)
Maximum $J_{IC}$ (Between Regimes II & III)	135	199 (1150)	-75	311 (1800)
Max. $J_{IC}$ /Min. $J_{IC}$	--	0.33 (1.9)	--	0.48 (2.8)

According to these tentative results, the transformation toughening has improved the  $J_{IC}$  toughness by a factor of 2-3. The amount of transformation which causes this toughening is relatively small (quantitative measurements are being made). Larger amounts of transformation reduce the toughness (Regime III).

presumably because the beneficial influence of the displacive transformation is counterbalanced by the lower toughness of the martensitic product itself.

It may be noted in passing that the volume change in this transformation is only about +2%, thus indicating that the shear component of the transformational displacement plays a more important role in the toughening than does the dilatational component. The magnitude of the volume expansion can be varied by appropriate changes in alloy composition, and so the effect of the dilatational component is amenable to more detailed investigation.

V-9. SOME USES OF CONTROLLED POROSITY TO IMPROVE CRACK  
PROPAGATION BEHAVIOR OF BRITTLE MATERIALS

E. E. Hucke

A shaped, spatially uniform, fine (0.1 to 5  $\mu\text{m}$ ), continuous pore non-crystalline carbon skeleton can be produced from a liquid polymer and then reacted with silicon to produce a fine (0.1 to 5  $\mu\text{m}$ ) SiC structure also containing a continuous silicon phase in the range 5-20%.

Because of the volume expansion on freezing and to the lower thermal expansion of Si relative to SiC, the resulting SiC structure is stressed in tension at low temperature which detracts from both the strength and toughness. When the Si pores are very fine ( $<0.1 \mu\text{m}$ ) and uniform, the freezing expansion often ruptures the structure giving Si-filled cracks of macroscopic dimension. A few larger pores (50  $\mu\text{m}$ ) will allow the Si to exude to the surface but the relatively large Si then becomes structural defects that adversely affect strength.

It has been possible to produce uniform, crack free fine grained material with good room temperature strength ( $>700\text{MPa}$ ) and toughness  $> 4.00 \text{ MPa}\cdot\text{m}^{1/2}$ . These values exceed those for commercial reaction bonded SiC, sintered  $\alpha$ -SiC, and approximately equal to those for hot pressed SiC.

The surface damage tolerance can be substantially improved by etching the free silicon network from the surface of the sample. Very uniform etched layers of controlled depths

ranging from a few micrometer to several millimeters can be produced. Even very thin etched layers raise the load required to give propagating cracks from a Vickers hardness indenter. The unetched structure gives cracks at  $< 1$  kg while a  $\sim 30 \mu\text{m}$  layer raises this value to more than 10 kg. The hardness is not very much affected by such thin layers. Layers  $\sim 100 \mu\text{m}$  deep raise the critical cracking load above 20 kg. These layers are quite successful in limiting the fracture to crushing under the indenter. In addition to providing pore volume, the removal of the Si presumably reduces the residual tensile stresses in the SiC which should benefit both strength and toughness. Thicker layers should also be beneficial in reducing damage due to finish grinding.

Additional effects are made possible by plating metal layers (eg. Ni, Cr) on to the etched surface. Subsequent heating causes a wetting of the plated layer into the pores as it melts and alloys with Si from the interior of the sample. The depth of zone and composition of the material in the surface pores are controlled by the original etch depth and plating thickness. Such a layer reduces the residual stress in the interior by removing Si and gives metal silicides in the surface pores. These silicides have thermal expansion coefficients greater than SiC and therefore stress it in compression on cooling to room temperature. The resulting layers have more than doubled the indicated fracture toughness of the material.

## V-10. ELASTIC SIZE EFFECT IN MICROSTRUCTURAL DESIGN

E. E. Hucke

In the design of microstructures of advanced materials the stress distributions near second phase inclusions ranging from ~100nm to 10nm are calculated using the elastic constants of the bulk phases. There is some experimental evidence that the Young's modulus of fine ceramic and glass fibers and whiskers increases as the diameter decreases. These data are not always easy to interpret because of structural changes that could occur as size changes. There are also data showing environmental influences on the elastic modulus of small specimens.

One possible explanation of a fundamental size influence on elastic properties can be made by a simple argument based on the surface modulus of elasticity. Under conditions of low temperature relative to diffusion, the surface stress of solids may differ significantly from the surface energy. A simple illustration shows that the observed modulus of a small sample should show a dependency on  $1/D$ , where  $D$  is the diameter of the sample.

Consider a long, round, elastically isotropic sample originally in mechanical equilibrium with its external surface. It is then loaded with an external force of  $F_a$ , perpendicular to its axial cross-sectional area  $A$ . There is in both surface and bulk an axial elastic strain of  $\epsilon$ . The applied stress,  $\sigma_0 = F_a/A$  is related to the observed elastic modulus

$$\sigma_a = E_o \epsilon$$

The applied stress is balanced by a bulk stress

$$\sigma_\beta = E_\beta \epsilon$$

and a surface stress,  $g$  (force per unit length of perimeter,  $P$ ). The surface stress is related to surface strain by a surface modulus  $E_s$ ,  $g = E_s \epsilon$ . An axial force balance at strain  $\epsilon$  yields

$$\sigma_a A = \sigma_\beta A + gP$$

Assuming linear elastic behavior

$$E_o \epsilon A = E_\beta \epsilon A + E_s \epsilon P$$

or

$$E_o = E_\beta + E_s (P/A)$$

For a circular sample

$$E_o = E_\beta + \frac{4}{D} E_s$$

At some value of  $D$  the second term should be important and may explain some of the experimental results. If this effect is appreciable, elastic stress distributions around small particles (or holes) must be modified.

## V-11. SOME EFFECTS OF PHASE TRANSFORMATIONS ON TOUGHENING

A. Evans

It is now well-established that phase transformations cause crack shielding and provide a contribution to the toughness given by:

$$\Delta K_C = 0.22 E e_f^T \sqrt{h} / (1-\nu)$$

where  $e_f^T$  is the dilatation in the transforming material of volume fraction  $f$ ,  $E$  is Young's modulus and  $h$  is the transformation zone width. This toughening superposes on the crack growth resistance of the transformed material ahead of the crack. In ceramics, the transformed product has essentially the same toughness as the parent phase and  $\Delta K_C$  represents the net toughening. However, in some metallic systems, wherein brittle martensites are found, the intrinsic crack growth resistance of the product may counteract the shielding and produce a net toughness degradation. Consideration of these two effects often permits interjection of toughness trends in materials subject to stress-induced transformations.



USE OF LONG WAVELENGTH NEUTRONS  
FOR EVALUATION OF VOIDS IN STRESSED SOLIDS

B. B. Rath

A better understanding of fracture behavior of metals and alloys has been essential because of an increasing need for designing crack tolerant structures for defense applications. Although the macroscopic character of fracture as a function of various stress states under conditions of either plane-strain or plane-stress has been extensively evaluated, microstructural mechanisms of void nucleation and their subsequent growth as a function of various metallurgical parameters have not yet been well-understood. The lack of a knowledge base is perhaps in part due to experimental difficulties in the direct observation of void nucleation events as a function of stress states.

Electron or optical microscopic examination has not provided clear insight on the effects of various metallurgical variables on the nucleation and growth of voids and how these influence plastic instabilities in alloy systems.

Recent studies have shown that scattering of neutrons is a sensitive function of the density of voids or cavities in solids. Voids in the size range, varying between 5nm and 100 nm can be quantitatively evaluated from small angle neutron scattering profiles. Although the analytical tools are the same, the neutron scattering method is significantly more advantageous compared to the x-ray method because of its high depth

of penetration and the absence of multiple Bragg scattering phenomena. With the use of an appropriate algorithm, the neutron scattering profile yields void size distribution histograms, essential to our understanding of void formation.

A number of systematic investigations can now be developed to study the effects of strain and strain rates on void size and distribution in a well characterized alloy system.

Metallurgical variables such as (1) equiaxial grain size and test temperature, (2) elongated grains with varying aspect ratios obtained by varying rolling reductions followed by a recovery anneal, (3) varying volume fractions of a second phase fabricated by composition variations in a model binary alloy system, (4) crystallographic texture (sharp single-component vs. random texture), (5) bond strengths and size variations of inclusions (strong and weakly bonded inclusions such as carbides and oxides of similar sizes can be blended with the base metal or alloy powder and consolidated with inclusion type and size variations), (6) grain boundary carbide thickness in the Fe-C system, and (7) varying hydrogen concentrations in Fe- and Ti-base alloys and their effects on void nucleation, size and population can now be systematically studied. Results of these critical experiments will provide the necessary formations relating  $J_{IC}$  with  $\sigma_0$ ,  $\epsilon_f$ , and  $l_0$  and other relevant parameters.

A. G. Evans, J. W. Hutchinson and B. Budiansky

Experimental studies of void nucleation at inclusions do not provide general implications concerning effects of inclusion size. The most comprehensive studies (Argon, et al) indicate that inclusion size is unimportant at small volume concentrations ( $\sim < 0.01$ ) of Cu/Cr inclusions in Cu and TiC inclusions in a maraging steel. In this range, void nucleation occurs at an interface stress,  $\sigma_i \sim 10^{-2}E$ . A size effect appears to develop at larger volume concentrations of inclusions ( $\sim 0.1$ ); at least for Fe<sub>3</sub>C inclusions in a spheroidized 1045 steel. Specifically, a preference for void formation at large, closely spaced inclusions was noted.

Several mechanisms of void nucleation at inclusions have been suggested. Equiaxed particles generally nucleate voids by firstly creating a separation at the interface. Inclusion cracking can also precede void formation, especially at elongated particles. The stresses needed to create the separation (or crack) are generally dictated by the plastic strain in the matrix. A size dependence of void formation involving brittle fracture of the inclusions may then, of course, be qualitatively interpreted in terms of a statistical distribution of flaws; but the presence of significant flaw distributions within inclusions of the appropriate size ( $\leq 10 \mu\text{m}$ ) is debatable. More generally, void nucleation will be dictated by the amplitude and scale of the tensile stresses that develop at the inclusion interface.

The stresses  $\sigma_i$  that develop at the interface of isolated spherical inclusions exhibit a maximum along the axis of principal applied tension and can be approximated by (Argon, et al)

$$\sigma_i = \sigma_0(\gamma_p) + \sigma_T \quad (1)$$

where  $\sigma_0$  is the flow stress,  $\gamma_p$  is the plastic strain and  $\sigma_T$  is the hydrostatic component of the applied tensile stress. The interface stress can be magnified between closely spaced inclusions. An upper bound stress can be obtained from the plastic strain that develops by prohibiting flow into the matrix between the inclusions,

$$\epsilon_p = (\gamma_p/2)(1-2\ell/\lambda)^{-1} \quad (2)$$

where  $\gamma_p$  is the shear strain,  $\ell$  is the inclusion radius and  $\lambda$  the inclusion spacing. Plastic strain concentrations of this magnitude are most likely in the presence of appreciable tri-axiality. The concentrated plastic strain results in peak interface stresses

$$\sigma_i \approx \frac{\sigma_0(\gamma_p)}{(1-2\ell/\lambda)^n} + \sigma_T \quad (3)$$

where  $n$  is the work hardening coefficient.

The interface stress thus exhibits important dependences on the plastic strain, the work hardening coefficient, the tri-axiality and the local volume concentration of particles (as

manifest in  $\lambda/\lambda$ ).<sup>#</sup> Invoking a void nucleation criterion based on a critical value of the interface stress thus anticipates coupled effects of plastic strain, triaxility and the local inclusion volume concentration. Size effects are not directly involved. A size effect could emerge if the distribution in  $\lambda/\lambda$  exhibits an absolute dependence on inclusion size.<sup>#</sup> Such size trends (undoubtedly dependent upon the inclusion coarsening mechanism) have not been studied. cursory inspection of typical particles does not reveal a systematic influence of size upon  $\lambda/\lambda$  (i.e., there are as many closely spaced small inclusions - large  $\lambda/\lambda$  - as closely spaced large particles). Careful studies of particle spacing trends are central to the interpretation of nucleation size effects predicated on a critical nucleation stress.

Analogy with size effects in the separation of brittle inclusions from brittle matrices suggests that a critical interface stress may be an inadequate criterion for void nucleation. A local stress intensification, at facets or interface defects that scale in size with the inclusion radius\*, may be more pertinent. Then an effective critical stress intensity factor,

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<sup>#</sup>The absolute particle spacings or sizes are not involved, contrary to the proposal by Argon, et al, only the relative spacing distribution is important.

\*Faceting results in logarithmic singularities at facet corners. The scale of the stress field (at the interface) thus depends on the facet length and hence, the inclusion size. A suitable product of the scale and amplitude of the stress determines the stress intensity factor.

$K_C^{eff} \approx \sigma_i \sqrt{l/2}$ , dictates interface separation, as expressed by the critical radius,

$$l_C \approx 2(K_C^{eff})^2 \sigma_0 (1 - 2l/\lambda)^{-n} + \sigma_T \quad (4)$$

The separation of interfaces characteristically occurs for  $K_C^{eff}$  in the range 0.5-2 MPa $\sqrt{m}$ . First order estimates of the critical size may be deduced from equation (4).

A second size effect exists when the inclusions are very small; viz, a minimum size below which void formation is prohibited. This minimum size is based on the requirement that the strain energy be of sufficient magnitude to provide the energy of the separated surfaces (Argon, et al). Formation of the void surfaces requires release of a proportion of the strain energy accumulation around the elastic inclusion. A prerequisite for void nucleation is thus;

$$(4/3)\pi\alpha l^3 (\sigma_i^2/2E) > 4\pi\beta l^2 \chi_f \quad (5)$$

where  $\chi_f$  is the fracture energy associated with void formation ( $\chi_s - \chi_i$  is a lower limit),  $\alpha$  is that fraction of the total available strain energy (around the particle) released during void formation and  $\beta$  is the fraction of inclusion surface that separates. The predicted critical size is sensitively dependent upon the values of  $\alpha$  and  $\beta$ . Argon, et al<sup>1</sup> assume that  $\alpha$  and  $\beta$  are unity.\* The detailed analysis needed to compute these

---

\*With  $\alpha$  and  $\beta$  unity, Argon estimates the critical value of  $l$  for decohesion as  $\sim 20$  nm. With a "cap-shaped" crack nucleus,  $\beta < 1$  and values as small as  $\sim 1$  nm are obtained.

quantities has not been performed and hence, literature estimates must be regarded as approximate.

Certain inclusions are subject to planar slip (e.g., manganese sulfide); size effects in such instances are directly explicable in terms of conventional dislocation pileup concepts, (Cox and Low). Also see article by Hirth, (1982 Report) when pileup spacings are small compared to  $2l$ , pileup stresses can be magnified, leading to a size effect. Pileup considerations are not discussed here.

#### ACKNOWLEDGEMENT

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#### REFERENCES

1. A. S. Argon and J. Im, Met. Trans., 6A, (1975) 839.
2. T. B. Cox and J. Low, Met. Trans., 5, (1974) 1457.

ROLE OF MICROSTRUCTURE IN INFLUENCING  
FATIGUE CRACK PROPAGATION

R. O. Ritchie

Based on our recent studies (i.e., with Suresh, Dutta, etc.) and those of others (i.e., McEvily, Beevers, Williams, Starke, etc.), it is apparent that increasing resistance to crack growth by fatigue can be most effectively achieved at lower growth rates (i.e., below  $\sim 10^{-5}$  mm/cycle in the near-threshold regime which dominates lifetime) by promoting mechanisms of crack closure. In addition to Elber's well known plasticity-induced closure, we have identified mechanisms arising from corrosion debris (oxide-induced), irregular crack paths (roughness-induced), viscous fluids inside the crack and phase transformations. With regard to the role of microstructure, the roughness-induced mechanism appears the most promising where exceptionally slow growth rates (and very high  $\Delta K_0$  thresholds) can be achieved through promoting a meandering crack path. Microstructures which i) show coarse planar slip (e.g., underaged Al alloys) or ii) sources of crack deflection (e.g., dual-phase structure), for example, are particularly beneficial, as shown in the present results for duplex martensitic/ferritic mild steels where we have obtained the highest  $\Delta K_0$  values reported to date for ferrous materials and furthermore by far the highest combination of yield stress and  $\Delta K_0$ . However, since such microstructure effects arise from an extrinsic mechanism (i.e., closure) which affects the crack driving force rather than the



inherent crack growth resistance, such superior resistance to fatigue (crack growth) will not be seen where closure is unimportant. Hence, for fatigue crack initiation, short cracks, S/N curves and fatigue crack growth at high mean stresses (i.e., high load ratios), such closure mechanisms will be much less effective.

J. C. Williams

In alloys which have complex microstructures it may be useful to consider the events which occur during crack extension and the role that these events have in affecting the resistance of a material to crack extension. From fractographic studies it is known that fractographic features with two or more size scales are commonly observed. The large scale features occur with dimensions on the order of  $\sim 10 - \sim 250 \mu\text{m}$  whereas the other, smaller features are typically  $< 1 \mu\text{m}$ . The large features are associated with crack deflection on reorientation whereas the small features appear to be related to the localized fracture process(es) which occur during crack extension. Both of these processes, crack deflection and local extension, contribute to the energy dissipated during crack propagation. The total energy must be some type of product of the two terms, maybe of the form:

$$J_R = A(J_{\text{upe}} \cdot J_{\text{path}}).$$

Here  $A$  is a constant of units  $\frac{1}{J}$  to make the proportionality dimensionally consistent,  $J_{\text{upe}}$  is a unit propagation energy term related to the local crack extension process and  $J_{\text{path}}$  is the contribution to  $J_R$  due to crack deflection. Since, in principle,  $J_{\text{upe}}$  and  $J_{\text{path}}$  can vary independently, the effective  $J_R$  must be a product of the two terms. For example, irregular fractures which follow a selected and tortuous brittle path will

be very rough but the  $J_R$  will be small because  $J_{Upe}$  is very small. In actual practice  $J_R$  is usually increased by increasing  $J_{path}$  under conditions of more or less constant  $J_{Upe}$  which is determined by the work hardening ability, and type of strengthening dispersion which is present and the deformation character of the matrix.

Accordingly a tough microstructure might contain the following features:

- A uniform distribution of preferred crack paths which have large enough  $J_{Upe}$  that the product of  $J_{path}$  and  $J_{Upe}$  is greater. If the  $J_{Upe}$  along these paths is too small  $J_R$  does not increase. Also, if the  $J_{Upe}$  is too large then other, weaker paths will be activated.
- A uniform distribution of small tightly bonded particles which are not shearable. These particles should elevate the work hardening rate so as to increase  $J_{Upe}$  and yet lead to large enough values of  $\epsilon_N$  (strain to nucleate voids) to also be consistent with a large  $J_{Upe}$  value.
- Low volume fraction of inclusions. The lower the volume fraction, the more uniform the spacing, the more equiaxed the inclusions, the less chance there is for these to lead to early void formation and enhancement of strain localization between the voids.

While the foregoing is qualitative or conceptual in nature it does help provide a basis for considering the complementary role of the two scales of fracture features commonly

observed in high strength alloys. It may also provide some insight into the relative roles of local fracture energy and the (somewhat) independent role of crack path tortuosity.

## DUCTILE FRACTURE

John W. Hutchinson

At high stress triaxiality (i.e., high values of the ratio of mean stress to effective stress), typical of that encountered at the tip of a plane strain crack or even at the center of a necked tensile specimen, it is frequently observed that essentially all the void growth in a high strength steel takes place on the fracture surface. Off the fracture surface voids are either not nucleated or undergo little growth if they are nucleated. This suggests that either (i) nucleation of voids triggers localization of deformation confining void growth to the fracture surface, or (ii) shear band localization sets in prior to void nucleation and then the intense shearing results in void nucleation in the band. We will assume that any relatively large inclusions, if present, have too small a volume concentration to play any significant role in the fracture process. Small second phase particles are assumed to have the major influence on the fracture process.

If it is supposed that (i) holds, then at a sufficiently high volume fraction  $f$  of second phase particles the fracture strain (for a given level of stress triaxiality) will be independent of  $f$ . That is, once enough particles are present to trigger localization at nucleation adding more particles will not effect the process. Qualitatively, the relation of fracture

strain  $\epsilon_f$  to volume fraction  $f$  of void nucleating particles is expected to be of the form shown in Fig. 1. For a given nucleation strain  $\epsilon_N$  let  $f^*$  be the minimum volume fraction of second phase particles needed to trigger localization at nucleation, and assume a relation between  $\epsilon_N$  and  $f^*$  such as that shown in Fig. 2. The curve of  $\epsilon_N$  vs.  $f^*$  divides the parameter space of  $(\epsilon_N, f)$  into two regimes corresponding to nucleation controlled and growth controlled fracture. In the nucleation controlled regime, diminishing  $f$  has little effect on the fracture strains, while in the growth controlled regime the fracture strain is sensitive to  $f$ .

If shear localization triggers void nucleation and subsequent void growth, it is again true that the fracture process should not be much affected by  $f$  as long as it is sufficiently large. A delay in strain localization will have more effect on increasing the fracture strain than an increase in the bonding strength of the particles.

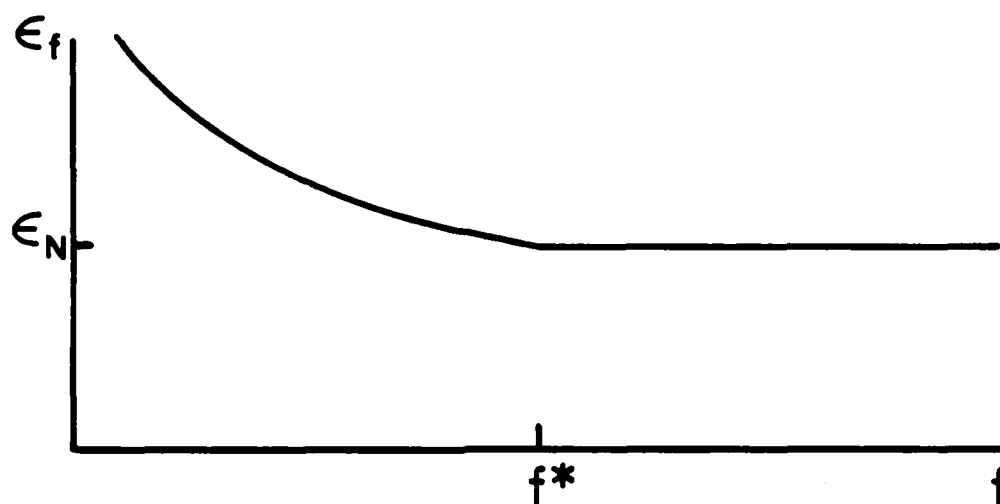


Figure 1. Fracture strain vs. volume fraction of void nucleating particles assuming voids nucleate at strain  $\epsilon_N$  and that void nucleation triggers localization for  $f \geq f^*$ .

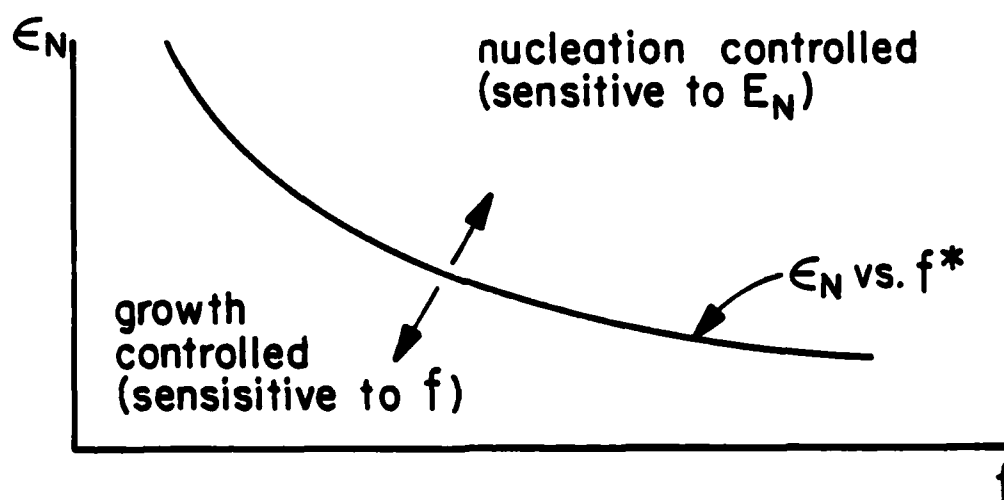


Figure 2. Schematic of regimes of growth vs. nucleation controlled ductile fracture.

MICROMECHANICS OF CLEAVAGE AND  
AND THE DUCTILE-BRITTLE TRANSITION

John W. Hutchinson

Recent work on the microscopy of cleavage fracture in steels has helped to clarify the way cleavage cracking at the microscopic level leads to macroscopic crack advance. Cracking of a brittle phase, such as a grain boundary carbide, can cause a cleavage crack to propagate across a grain if local stress conditions are sufficiently intense. At temperatures well below the ductile-brittle transition the nucleation of such a cleavage crack appears to be the critical event with the running cleavage crack continuing into the contiguous grains and beyond. In many steels few, if any, stable grain-sized micro-cracks are observed at low temperatures. The fracture toughness model of Ritchie, Knott and Rice applies in this temperature range. It assumes a microscopic cleavage stress and a characteristic distance over which this stress must be attained for macroscopic crack advance to occur. These quantities are assumed to be temperature-independent (or nearly so), and the temperature variation of fracture toughness is determined from the model in terms of the corresponding variation of the yield stress with temperature.

Early work of Hahn, Averbach, Owen and Cohen and by Cohen and Vukceovich on tensile ductility of steels over a wide temperature range showed that a multitude of stable grain-sized micro-cracks are generated in a range of temperatures in the



vicinity of the transition. Well below the transition few such cracks are observed because, as already discussed, essentially the first micro-cracks to be nucleated are unstable and lead to macroscopic fracture. Well above the transition it appears that no micro-cracks are nucleated, for reasons that are not entirely clear. In the transition range, macroscopic fracture involves a complicated interaction between micro-cracks which is not even qualitatively understood.

Discussion by Hoagland, Rosenfield and Hahn and more recently by Irwin and coworkers on the behavior of steels in the lower transition range suggests that most of the fracture energy is associated with plastic deformation and failure of the connecting ligaments between cleavage facets. In effect, the critical cleavage stress increases with increasing temperature in the lower transition. It is possible that the characteristic length introduced in the model of Richie, Knott and Rice may also have to be regarded as an increasing function of temperature. Micro-mechanical modeling of fracture toughness (and stable crack growth) in and near the transition remains to be accomplished.

#### ACKNOWLEDGEMENT

This report was written under the auspices of the DARPA Materials Research Council, Contract #MDA903-83-C-0349 with The University of Michigan.

VI.

AGENDA

WORKSHOP ON MICROSTRUCTURE AND TOUGHNESS

July 18-19, 1983

JULY 18

8:30 AM	S. Fishman
8:55 AM	E. Hucke
9:20 AM	J. Hutchinson
9:45 AM	A. Miller
10:40 AM	D. Drucker
11:05 AM	A. Evans
11:30 AM	A. Rosenfield
1:00 PM	J. Hirth
1:25 PM	E. Starke
1:50 PM	M. Cohen
2:15 PM	A. Thompson
3:00 PM	J. Williams

JULY 19

8:30 AM	Discussion lead by J. Hutchinson & A. Evans
10:30 AM	Discussion lead by J. Hirth & J. Williams
1:00 PM	General Discussion & Wrap-Up Chaired by D. C. Drucker
3:00 PM	Closing Remarks
3:30 PM	Adjournment

LIST OF PARTICIPANTS  
WORKSHOP ON MICROSTRUCTURE AND TOUGHNESS  
July 18-19, 1983

B. Budiansky	Harvard
M. Cohen	MIT
A. Cooper	Case-Western Reserve U
G. Dieter	Univ. of Maryland
D. Drucker	Univ. of Illinois
A. Evans	Univ. of California
S. Fishman	DARPA
J. Hirth	Ohio State Univ.
E. Hucke	Univ. of Michigan
J. Hutchinson	Harvard
W. Isler	DARPA
T. Kearns	IDA
R. Lewis	Lockheed
D. Marshall	Univ. of California
A. Miller	Stanford
R. Mehrabian	NBS
R. Ritchie	Univ. of California
A. Rosenfield	Battelle
W. Snowden	DARPA
A. Thompson	Carnegie-Mellon Univ.
B. Wilcox	NSF
J. Williams	Carnegie-Mellon Univ.

## WORKSHOP ON SPACE MATERIALS

G. H. Vineyard and H. Ehrenreich

A day and a half workshop on materials for space systems was held July 25 and 26, 1983.\* Introductory talks were given on problems in the areas of power systems (primarily solar photovoltaics and nuclear reactors), space structures, and coatings for space structures. Durability of materials against radiation and the oxygen plasmas in space was discussed, and survivability against space weapons, particularly lasers and nuclear weapons, was considered at several points, although the unclassified character of the meeting precluded going beyond generalities on survivability. Observability of space systems was also discussed briefly and in general terms.

Near the end a general discussion of pressing needs and special opportunities for advances in space materials was conducted, and opinions from the visiting consultants and lecturers were solicited and debated.

Obviously the topic is huge and the treatment that could be afforded in such a short meeting was superficial and very incomplete. Primarily the meeting was meant to be an introduction for the Council which may be followed up by more detailed work in narrower areas at a later date. Nevertheless a number of observations and recommendations were generated, and these are recorded here.

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\* The attendance list and program are appended.

## SOME OBSERVATIONS

1. The SP-100 program to develop a nuclear reactor power plant for space at the 100 kW level is, by admission, only in its early phase and therefore not enough work has been done to form much of an idea of critical materials problems. It is intended to have this kind of information by 1985. Nevertheless it is obvious that a large range of materials limitations will bound performance. Critical materials will include high temperature alloys and ceramics employed in the fuel, the in-core structures, the heat transfer system, the heat conversion system, and the radiators. High strength materials operating at temperatures in excess of 1000°C and in an intense radiation environment are needed, which stretches the available technology. High temperature strength and creep properties of refractory alloys have not even been measured to the extent that is needed, and vigorous prosecution of existing or new programs on high temperature materials is very much in order. Much of the information available comes from the nuclear rocket program, which was terminated several years ago. Existing high temperature materials studies seldom are concerned with a radiation environment, and reactor-oriented materials work is today at a low ebb. More exotic refractory alloys, including the elements Ta, Mo, Hf, Nb, and W need to be looked at in some detail.

2. Beryllium has the attractive properties of very low atomic number and density, together with moderately high refractoriness. It has apparently been given rather little

attention as a structural material, primarily because of its brittleness. The possibility of increasing its ductility by RSR processing is being explored and holds promise. There may also be beryllium alloys which are less brittle and which have better resistance to creep at higher temperature. A promising field for exploration would be the combination of alloying with RSR processing.

3. Photovoltaics are most desirable for low power systems (<30 kW) and are superior in that range to nuclear sources because

- a) there is greater experience with PV power systems in space (about 25 years) and therefore they have greater reliability;
- b) such systems (even including battery storage) may be lighter. The energy quality (as measured by the entropy) produced by a PV array is higher than that of a nuclear source;
- c) fewer moveable parts and no piping carrying hot corrosive liquids are involved (for example, heat pipes carrying Li.);
- d) they have public acceptability.

4. Nuclear Power probably will be advantageous for spacecraft involving higher levels (> 100 kW). This is associated with the compactness of a reactor relative to that of an equivalently powered solar array and the need for maneuverability.

5. Despite the extensive experience with Si and its proven reliability in space applications, GaAs, or tandem cells involving it, may well turn out to be the material of choice. In part this is associated with the higher efficiencies achievable with GaAs, its self-annealing properties even at temperatures of 100-200°C, and the fact that the needed thicknesses of cell material are considerably less than that of Si. The total cumulative effects of radiation damage, even in the presence of annealing, have not yet been fully evaluated. Furthermore, annealing procedures would pose problems for tandem cells associated with diffusion. However, the possibility of success appears to be sufficient to justify a research program directed at developing a GaAs based PV technology for space.

As a follow-up, a research program aimed at developing GaAs concentrator systems for space, and another program directed towards the achievement of a robust tandem cell, consisting perhaps of GaAs and Si, might be contemplated. The efficiencies of such systems may be expected to be in the 20-30% range.

6. The possibility of hybrid systems combining PV with a nuclear reactor or other high-level power source for intermittent high level operations may deserve exploration.

7. Composite materials, including metal matrix and ceramic matrix materials, will undoubtedly play an increasing role in space. Emphasis on low atomic number imposes a new selection criterion, and a number of systems under study are meritorious in this regard. Graphite/magnesium has the additional advantage

of very low thermal expansion, but the disadvantage of a low limiting temperature. Many other combinations appear to warrant further R & D. Beta silicon carbide is a very promising fiber, and boron nitride, which has had little attention, is another. Carbon/carbon materials in various forms are attractive because of low density and atomic number combined with toughness, strength, and resistance to high temperatures. These are under development and warrant increased attention.

8. Coatings whose absorptivity can be controlled by a voltage applied to a thin conduction layer on the surface of the coating were described by one participant. These might be very useful in controlling heat balance, as well as for purposes of deception, if developed sufficiently. It appeared to us that there are other materials, such as some conducting polymers, which were not considered and which might have an advantage over the ion-transport systems proposed, particularly by allowing a great reduction in the response time, which was of the order of 20 minutes for the materials described at the workshop.

Another possibility suggested by one MRC member (Wrighton) is control of reflectivity by the reversible electro-deposition of a shiny metallic layer (such as silver) at the base of a layer of transparent electrolyte.

9. Weight is an extremely important consideration, of course, in all space systems, even more so in systems that must be sent to higher altitudes or in systems that must have rapid maneuverability. Lighter batteries, which were discussed at



another MRC workshop this summer, could help a great deal. Further advances could be made in the materials for the wiring harness for PV arrays (the harness now makes up a surprisingly large fraction -about 25%-of the weight of a large PV system). In addition to increasing the voltage of the system, using lighter conductors such as intercalated graphite could help substantially. We believe that NASA is mounting an R & D program on this, but if it is not we believe DARPA should.

10. Hardening against laser attack imposes further constraints which were considered only briefly in this workshop (laser hardening was considered more at length at other meetings this month). Many of the composite materials which are structurally desirable have some resistance to this threat and research is being done to improve resistance by coatings and impregnation. Continued effort of this kind is obviously important.

11. Low visibility to radar requires methods which were discussed in the RAM/RAS meeting. Methods applicable to aircraft are also applicable to spacecraft, with the complication that emissivity control and laser hardening are simultaneous needs in spacecraft.

12. A special problem in spacecraft is the need to control the volatility and outgassing of all components that become heated (particularly engines, thrusters, and heat sinks) because this can contaminate optical surfaces on the craft. This is a consideration that ordinarily does not concern the materials

engineer and requires attention in connection with the various new materials being proposed.

#### RECOMMENDATIONS

1. In addition to the requirements for materials which are light, strong, refractory, etc., space uses demand materials with a number of other special properties. New forms of materials, particularly metal matrix and ceramic matrix composites offer considerable potential for meeting these needs but will require long range and intensive R & D to realize their potential. We recommend that DARPA support such work. This includes fundamental research to improve understanding of the relation of properties of composites to their structure.

2. Work on high-temperature alloys and ceramics must continue. The SP-100 program brings the additional problem of radiation damage in such materials. Information on this is inadequate and should be improved.

3. Gallium arsenide photovoltaics systems should be developed.

4. Electrically controllable coatings appear to offer useful possibilities. More research should be done here.

5. A program to develop lighter weight conductors for space photovoltaic systems should be undertaken.

#### ACKNOWLEDGEMENT

This report was written under the auspices of the DARPA Materials Research Council, Contract #MDA903-83-C-0349 with The University of Michigan.

MEETING ON  
SPACE MATERIALS

July 25-26, 1983

Monday, July 25

G.H.Vineyard, MRC/BNL	Introduction
F. Patten, DARPA	Satellite Considerations
J. Mondt, Jet Propulsion Lab	SP-100 Program Overview
H. Enrenreich, MRC/Harvard	Photovoltaic Status
H. Brandhorst, NASA	Photovoltaic Systems in Space
L. Cohen, McDonnell- Douglas	Space Structure Survivability
B. Rath, NRL	General Materials Capabilities
C. Chang, NRL	Thermal Expansion and Rigidity

Tuesday, July 26

T. Kramer, Boeing	Thermal Control Films
A. Gupta, NASA	Natural & Induced Environments
Discussion and Recommendations	

# SPACE MATERIALS ATTENDEES

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## ELECTROCHEMICAL ENERGY SOURCES

M. S. Wrighton

### INTRODUCTION

Electrochemical energy sources are presently used in many military devices. Demanding applications stimulated interest in having an MRC workshop on electrochemical energy sources. The aim of the workshop was to provide DARPA with input regarding scientific and technical opportunities for advancing the state of knowledge and development of batteries and fuel cells.

Batteries and fuel cells are devices for the direct conversion of chemical energy to electricity. The distinction between a fuel cell and a battery is that the fuel cell uses energy-rich materials that are added to the device, whereas a battery is a self-contained energy source that uses the energy-rich materials encased in it. Batteries are of two types: (1) primary (non-rechargeable) and (2) secondary (rechargeable).

At present, there is a large commercial U.S. market for both primary and secondary batteries, Table I, including  $\sim \$250 \times 10^6$  for the military market. There is no significant market for fuel cells, but large scale testing in utility applications is underway in the U.S. and Japan. Fuel cells are, however, used in space vehicles. The estimated spending for research and exploratory development by the battery industry is probably  $< 0.5\%$  of gross sales or  $< \$25 \times 10^6$ . In FY83 it is estimated that the total funds provided by the Department of Energy for battery and fuel cell research and development was  $\sim \$45 \times 10^6$ .

Table I. U. S. Market for Batteries in the United States\*.

<u>Primary Batteries</u>	<u>\$ in Millions Annually</u>
<u>Kind</u>	
Carbon/Zinc	400
Alkaline	325
Miniature	325
Military	<u>100</u>
	Total \$1175
<u>Secondary Batteries</u>	
Automotive (Starting, Lighting, Ignition)	2200
Industrial Motive Power	350
Portable	350
Stationary	250
Solar Storage	3
Military	<u>150</u>
	Total \$3303
Total U. S. Market: \$4378	

\*Source: R. Brodd. (For ~1980-1982 time frame.)

The DoD also has significant research programs; the ONR-supported program alone is  $\sim \$11 \times 10^6$ . These approximate data are included here to provide background and are not intended to be a precise measure of the U. S. commercial enterprise or research volume.

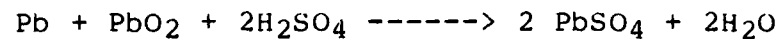
#### Basics of Electrochemical Energy Sources

In principle, any spontaneous, ( $\Delta G < 0$ ), chemical reaction can be exploited to directly generate electrical energy. Practical constraints, however, limit the chemical systems that can be regarded as useful. Among the criteria used in selecting chemical systems is the specific energy in watt-hours per kilogram, W·h/kg. In all portable electrochemical energy source applications the specific energy is of primary importance. It is this criterion that drives the interest in chemical systems that involve the use of low atomic weight elements that are reduced, e.g. Li, in combination with potent oxidants such as  $O_2$ .

The key equation is:

$$-\Delta G = nFE$$

where  $\Delta G$  is the free energy change,  $n$  is the number of electrons involved,  $F$  is the Faraday, and  $E$  is the cell voltage. This equation is system specific and fixes the cell voltage and the net available energy. The theoretical specific energy can be determined by dividing  $-\Delta G$  by the mass of the reactants. For example, the net cell reaction in a lead acid cell is given by:



where  $E=2.095\text{V}$  and the theoretical specific energy is  $175 \text{ W}\cdot\text{h}/\text{kg}$ . Table II gives additional examples of the theoretical specific energy for several systems.

The theoretical specific energy cannot be achieved in practice, owing to the penalty associated with the mass of packaging materials, solvent, electrolyte, etc. Indeed, the demonstrated specific energy for most batteries falls at least a factor of four below theoretical. The realized specific energy is thus not only a function of the energy producing chemicals but is also sensitive to overall design and the materials used therein. The lead acid battery has been demonstrated to have a specific energy of  $30\text{-}40 \text{ W}\cdot\text{h}/\text{kg}$  at a specific power of  $10 \text{ W}/\text{kg}$ . The specific power is a measure of the rate of energy delivery per unit of mass and is controlled by the rate of the energy-releasing chemical reactions and the overall design.

Aside from the criteria of energy available per unit mass and the rate at which it can be delivered is the additional criterion of size. While the density of the energy-rich materials places a limit on the size of a given electrochemical energy source, the size of batteries and fuel cells is a function of design and specifically desired characteristics.

A variety of practical considerations demand that batteries have some other features. Many of the features considered for secondary batteries apply to primary batteries as well; Table III. The main point is that a useful battery involves the



Table II. Theoretical Specific Energy for Some Battery Systems\*

System	Theoretical Specific Energy, W•h/kg
Zn/nickel oxide	
$\text{Zn} + 2\text{NiOOH} + 2\text{H}_2\text{O} = \text{Zn}(\text{OH})_2 + 2\text{Ni}(\text{OH})_2$	351
Cd/nickel oxide	
$\text{Cd} + 2\text{NiOOH} + 2\text{H}_2\text{O} = \text{Cd}(\text{OH})_2 + 2\text{Ni}(\text{OH})_2$	210
H <sub>2</sub> /nickel oxide	
$\text{H}_2 + 2\text{NiOOH} = \text{Ni}(\text{OH})_2$	443
Zn/Cl <sub>2</sub>	
$\text{Zn} + \text{Cl}_2 = \text{ZnCl}_2$	827
Zn/air	
$\text{Zn} + \text{H}_2\text{O} + 1/2\text{O}_2 = \text{Zn}(\text{OH})_2$	900
Li/air	
$\text{Li} + 1/2\text{H}_2\text{O} + 1/4\text{O}_2 = \text{LiOH}$	3900

\*Source: "Assessment of Research Needed For Advanced Battery Systems," Publication NMAB-390, National Academy Press, Washington, D.C., 1982.

Table III. Characteristics of Secondary Batteries

Ability to Recharge and Deliver Power  
Cycle Life  
Mechanical and Chemical Durability  
Self-discharge  
Over Chargeability  
Charge Time  
Shape of Discharge Curve  
Temperature of Operation and Storage  
Safety  
Cost  
Size  
Voltage

consideration of many factors beyond the redox reactions responsible for the generation of electricity.

Much of the foregoing discussion applies to fuel cells. At the present time, though, most of the activity in fuel cell research and development involves the exploitation of net reaction according to:



While the source of  $\text{H}_2$  may differ, the  $\text{O}_2$  is from the air as in metal/air batteries. A main limitation to fuel cells (and to metal/air batteries) is that the reduction of  $\text{O}_2$  at electrodes to form  $\text{H}_2\text{O}$  does not occur at a significant rate near the thermodynamic potential. Consequently, fuel cells operate at an output voltage considerably less than the thermodynamically predicted value of 1.23V. The interest in fuel cells in utility applications stems from the advantages over combustion of fuel for electricity generation, Table IV. Batteries have the same virtues, but do not use ordinary fuels and are generally viewed as storage or load levelling devices in a utility system.

#### WORKSHOP SUMMARY

A two day workshop on electrochemical energy sources was held on July 11 and 12, 1983 at the MRC meeting. The program and list of attendees are given at the end of this report.

M. Wrighton of the MRC organized the workshop. R. Reynolds indicated that the main purpose was to inform the DARPA/DSO of the state of the technology and to identify opportunities for

Table IV. Advantages of Fuel Cells and Batteries in Utility Applications.

High Theoretical Efficiency

- Not Heat Engine - No Carnot Limit
- Transmission Losses Can be Minimized

Low Noise and Air Pollution

Portable

No Moving Parts\*

Rapid Response to Large Changes in Demand

\*Assuming that pumps are not used to circulate fuels or electrolyte solution.

advancing it through new research effort. J. Smith of ONR gave an overview of the research program in electrochemistry in the Navy and indicated that the combination of 6.1, 6.2, and 6.3 programs involved  $\sim \$11 \times 10^6$  in funding per year. Typical battery applications of interest to the Navy are given in Table V and research and exploratory development areas supported by ONR are given in Table VI. W. Bishop of USAF/AFWL gave an overview of Air Force programs. The programs described are largely keyed to specific practical goals of direct military significance. Bishop noted that 6.1, 6.2, and 6.3 programs are supported by the Air Force, but focused on practical goals. Some representative programs taken from Bishop's view graphs are given in Table VII. The point to be made here regarding these programs is that there is a wide range of battery applications demanding very different performance characteristics.

R. Brodd surveyed the battery business in the U. S., Table I, and gave an overview of present practical battery systems. The discussion ranged from primary hearing aid batteries based on zinc/air to secondary lead acid batteries. Electrochemical power sources for electric vehicles were surveyed by E. Cairns. One of the main issues is that an electric vehicle can be very efficient relative to an internal combustion engine vehicle from the stand point of power train efficiency; Table VIII. The largescale commercialization of electric vehicles hinges in part on the efficiency of the utilization of primary energy sources, but for military purposes this may be of

Table V. Typical Battery Applications for the Navy\*

BUOYS	SONOBUOYS
TRANSPONDERS	SOUND SOURCES
ARRAY & CABLE SYSTEMS	DECEPTION DEVICES
BIOTELEMETRY	FIELD RADARS
MINES	LASER DESIGNATORS
TENDED ARRAYS	TORPEDOES
SEISMIC SENSORS	RADIOS
BALLOONS	MANNED SUBMERSIBLES
MISSILES	SUBMARINES
MEMORY BACKUP	AIRCRAFT

\*Source: J. Smith, ONR.

Table VI. Research and Exploration Development Areas Supported  
by ONR\*

(6.1) RESEARCH

- THEORY
- PROCESSES
- MATERIALS
- CHARACTERIZATION
- SOLID ELECTROLYTES
- FUTURE POWER SOURCES
- PRESENT POWER SOURCES
- SUPPORTING RESEARCH
- PHOTOELECTROCHEMISTRY

(6.2) EXPLORATORY DEVELOPMENT

- LITHIUM POWER SOURCES
- MOLTEN SALT BATTERY TECHNOLOGY
- OTHER BATTERY SYSTEMS

\*Source: J. Smith, ONR.

Table VII. Some Air Force Programs\*

- I. Objective: lightweight battery technology for year 2000 space power systems. Goal: 100 W·h/pound, 10 yr. life, 1000 cycles. 0.5 kW/pound.

Military Payoff: supports AFWAL SAMT. Weight reductions possible. Will permit realization of space power systems up to 100kW. Upper stage booster limitations will permit only 50kW with HEDRB technology.

- II. Objective: Long life, high power density rechargeable battery to meet peak radar and weapon loads. Goals: 0.7 kW/pound, 20 W·h/pound, 15,000 cycles, 10 yrs. life.

Military Payoff: Supports AFWAL SAMT. lower wt. power system for surveillance and weapon systems. Will save 860 pounds in a 100kW pulsed system.

- III. Objective: Lightweight noise filter for electrical power buses in pulsed power systems. Goal: 10 J/pound,  $10^9$  cycles at 50 Hz,  $10^8$  cycles at 5 Hz.

Military Payoff: Supports AFWAL SAMT. Future space systems such as radar will require noise-free bus power. Filter capacitors are forecast to deliver 1 J/pound. This technology will save 4500 pounds in a 50 kW, 5 Hz power system.

- IV. Objective: Power source technology to support non-conventional weapons. Goals: 3 kW/pound, 1000 sec total active life, 5 year calendar life.

Military Payoff: Supports AFWAL SAMT. Modular power source to support advanced weapons demonstrations up to 10 megawatts.

- V. Objective: High energy density, reserve battery for advanced strategic missile systems. Goals: 100/W·h/ pound, 6 W·h/in<sup>3</sup>, 0.5 hr. discharge rate, 1 kW/pound.

Military Payoff: Reduces battery weight by 45% over advanced Ag-Zn missile batteries and 150% over SOTA batteries.



Table VII. Con't

- VI. Objective: Demonstrate advanced reserve battery technology to meet the needs of long range tactical missiles attacking low observable targets. Goals: 10 kw/pound 300 sec life, AMRAAM battery wt and vol., no external power from carrier.
- VII. Military Payoff: Supports AFWAL night in weather and super sonic persistence major thrusts for longer life and higher output missile power sources. Provides longer missile range and ability to track very low signature targets.
- VIII. Objective: Ni-Cd battery state of charge on board aircraft. Goal: 5% accuracy from 10-90% full charge.
- Military Payoff: Support AFWAL sorties generation and supersonic persistence major thrusts as well as LN 182058. Provides direct indication of power capability of on board batteries, especially in uninterruptable power supplies.
- IX. Objective: 1-50 AH low maintenance batteries for a/c uninterruptable power systems. Goals: 1000 flt hr/3 yr maintenance interval.
- Military Payoff: Support AFWAL sortie generation and supersonic persistence major thrusts. Tenfold increase in maintenance interval, self contained diagnostics rapid recharge, autonomy, and uninterruptable fault tolerant a/c power. Supports AFLC needs for self test, monitoring, and elimination of field maintenance shops.

\*Source: W. Bishop, AFWAL.

Table VIII. Power Train Efficiency for Electric Vehicle  
Compared to Internal Combustion Engine Vehicle\*

<u>Internal Combustion Engine Vehicle</u>	<u>Electric Vehicle</u>
Thermal Efficiency = 20%	Battery Charge and Discharge
Mechanical Efficiency = 76.7	Efficiency = 73%
Transmission and Differential	Motor and Controls = 65-75%
= 92%	Motor Output to Wheels = 93%
<hr/>	
Power Train Efficiency = 14%	Power Train Efficiency = 44-51%

\*Source: E. Cairns, LBL.

Note: The emphasis here is to show the improvement in range of a vehicle employing conversion of fuel to electricity rather than fuel to heat as in the internal combustion engine powered vehicles.

secondary importance in many applications. For example, vehicle range might be more important than efficiency of utilization of primary energy sources. Cairns gave an overview of the state of batteries for electric utilities. Figure 1 shows a summary of various systems. D. Linder presented the status of primary Li batteries. While these are gaining acceptance and are beginning to be used there is still a need for attention to safety issues. Fuel cells were discussed by F. Anson. He identified improvement of the  $O_2$  electrode as a major research opportunity. Anson described the results from a collaborative project with J. Collman of Stanford to find electrode catalysts for the reduction of  $O_2$  to  $H_2O$  in acid media. A synthetic cofacial porphyrin, Figure 2, has been shown to be able to catalyze  $O_2$  reduction at a very positive potential and does not yield  $H_2O_2$ . The interesting point here is that the multi-electron reduction of  $O_2$  can be effected close to the thermodynamic potential without Pt as a catalyst. F. Will surveyed metal/air batteries and again emphasized the efficiency penalty associated with the  $O_2$  electrode.

Redox active, electronically conducting polymers were discussed in the presentation of A. MacDiarmid, L. Schacklette, and F. Will. Particular emphasis was on polyacetylene,  $(CH)_x$ . The topic generated spirited discussion regarding whether  $(CH)_x$ , or any other polymer, would meet the requirements for a battery. In view of the low atomic weight of C and H, the emphasis on  $(CH)_x$  is understandable in order to realize good specific energy, but the fraction of CH units oxidized or reduced must be

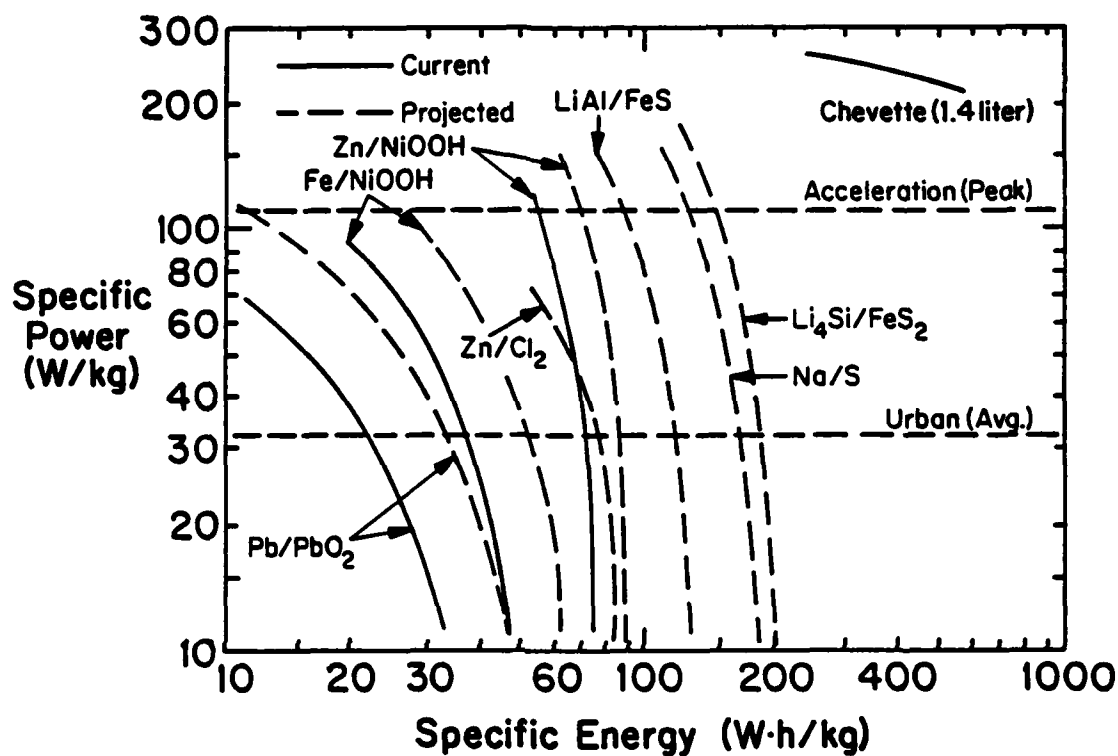
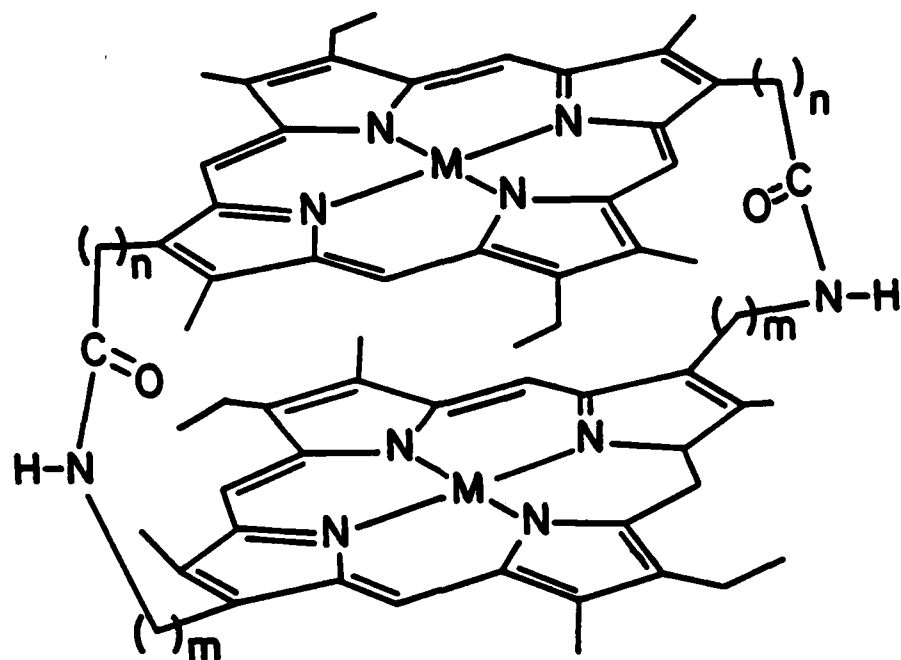


Figure 1. Comparison of Vehicle Propulsion Sources.



$M = M' = \text{Co}$

$n = 1$

$m = 1$

Figure 2. Electrode Catalyst for Reduction of  $\text{O}_2$  in Acid Media  
(from R. R. Durand, Jr., C. S. Bencosme, J. P. Collman, F. C. Anson, J. Am. Chem. Soc., 1983,  
105, 2710.)

significant to compete with polymers merely having pendant redox molecules. The electronic conductivity of  $(CH)_x$  upon oxidation or reduction is a significant advantage, but the lack of good electronic conductivity in a material does not rule out its use as an active material in a battery. MacDiarmid discussed recent demonstrations of the use of oxidized  $(CH)_x$  as an electrode in aqueous electrolytes. The interesting finding is that the material appears to be durable in strong aqueous acid.

G. Ramsay of Gould, Inc., presented some interesting results during the discussion period. He described work establishing the proof of concept for a new high rate, high energy density Li battery employing  $BrF_3$  as the oxidant. The (impure)  $BrF_3$  seemed to have sufficient ionic conductivity that no added electrolyte was necessary.

#### Generic Problems

The workshop revealed several generic problems associated with electrochemical energy sources. The following are ones that seem most common.

#### Electrochemical Kinetics

In batteries there is interest in achieving high rate (power). The rates can be limited by electrode kinetics. Fundamental studies of heterogeneous kinetics can lead to understanding of the rate determining step. Similarly, in fuel cells the kinetics for the electrode reactions are in need of improvement. The  $O_2$  electrode has already been mentioned in connection with both metal/air batteries and fuel cells. Additionally, the

fuel cells presently use  $H_2$  as the reduced material; direct use of liquid hydrocarbons or alcohols would require the development of new electrode catalysts. The improvement in electrode kinetics would give superior discharge curves. An understanding of the mechanisms of electrode reactions is imperative.

#### Rechargeability

Batteries that involve the oxidation of a metal during discharge can be recharged by re-depositing the metal electrochemically. The discharge/charge cycle must occur with retention of the electrode morphology in order to preserve performance. The lack of adequate metal regeneration is a problem common to all such systems. Such problems of rechargeability do not occur in fuel cells or redox batteries where the electrodes are inert. Also, it is possible that the batteries based on electroactive polymers would not have recharge difficulties. The drawback with the fuel cells and redox batteries is that the current collectors diminish specific energy. The Ni/ $H_2$  battery has excellent cycle life and is the battery to be used in satellites. This system avoids the Cd electrode problem of the Ni/Cd battery and has higher theoretical and demonstrated specific energy. However, the theoretical specific energy of the Ni/ $H_2$  battery, 443 W·h/lg falls far short of the best rechargeable metal/air batteries. Fundamental studies of metallic electrode reformation in the charge cycle would seemingly have broad impact on the technology of secondary batteries.

### State of Charge, Testing, and Evaluation

One of the continuing problems associated with batteries is the fact that the state of charge of a battery is difficult to assess. The analogue of a fuel gauge for batteries would be of practical value in minimizing replacement costs of primary batteries and in improving reliability. Additionally, non-destructive evaluations of batteries at the manufacturing site would improve the yield quality, and reliability. Impedance studies appear to be of value in this regard. New approaches to assessing the state of charge might include the utilization of advances in sensors such as ChemFET's. Non-destructive evaluation could include x-ray CAT scanning or possibly NMR imaging. It is likely that a conscious effort to implement new diagnostic procedures would prove fruitful.

### Design and Packaging

The achievable performance of batteries (specific energy, specific power, and peak power, for example) depends in large part on the design of the battery. Understanding of mass and charge transport in battery systems can yield valuable input for the design. For example, improvements in lead acid batteries have come from changes in the electrode grid design.

### Self-Discharge and Safety

A charged battery is thermodynamically unstable. Self-discharge is an important practical concern and can limit shelf-life. Catastrophic reactions can occur that raise safety and reliability issues. For Li batteries there seems to be a need



for fundamental understanding of the passivation layer on the Li, for example. Identification of the actual cell reactions for Li batteries is needed and both  $\text{SOC}_2$  and  $\text{SO}_2\text{Cl}_2$  systems require further study.

#### Membranes and Separators

Separators in many battery systems are critical elements. In  $\text{H}_2/\text{Cl}_2$  fuel cells for example, an expensive separator is needed to prevent mixing of the  $\text{Cl}_2$  and  $\text{H}_2$ . Separators of more and less sophistication with respect to selectivity are used in most electrochemical energy sources. There are opportunities for new materials. One should include solid ionic conductors such as polyethylene oxide or  $\beta\text{-Al}_2\text{O}_3$  as novel battery materials.

#### New Redox Systems

All batteries and fuel cells depend on thermodynamically downhill chemical reactions that can be broken into two half-cell processes to convert the energy released into electricity. While it may be obvious to attempt to exploit light, potent reductants such as Li in combination with light, potent oxidants such as  $\text{O}_2$ , there are non-obvious reactions and materials that could be useful. The proposed  $(\text{CH})_x$  battery based on the oxidation and reduction of the CH units is one example. Further, it is not always possible to actually do what is desired. For example, it is clear that in theory a Li/ $\text{F}_2$  battery would be desirable, but it is a non-trivial problem to be able to exploit  $\text{F}_2$  in an electrochemical energy source. In this same vein, even

the exploitation of Li is non-trivial inasmuch as immersion of Li into solutions of oxidants such as  $\text{SO}_2\text{Cl}_2$  runs counter to the instincts of experienced chemists. The point is that new ways to exploit energy dense materials and the discovery of new ones will lead to the next generation of battery systems.

#### RESEARCH OPPORTUNITIES

The participants of the workshop identified several priority areas of research. The discussion of the priority areas was divided into three sections: polymers, fuel cells, and the general field of batteries.

##### Polymers

In the area of polymers in batteries much of the discussion concerned  $(\text{CH})_x$  and poly-p-phenylene. It was noted that doped  $(\text{CH})_x$  is the best electronic conductor and has the lightest repeating unit of any conducting polymer. The following areas were identified as priority areas regarding  $(\text{CH})_x$ :

- Current collector and its contact
- Synthetic procedures for  $(\text{CH})_x$
- Durability vs. Dopant concentration
- Morphology, pore size
- Battery engineering
- Electrode structure

The battery engineering and electrode structure are areas common to all active polymers. Other areas deserving attention in the polymer area are new conducting polymers and the use of conducting phases in polymers having poor conductiv-

ity. Polymers also may play a crucial role as separators and solid state ionic conductors in batteries and fuel cells.

#### Fuel Cells

The development of better O<sub>2</sub> reduction catalysts is the key area in fuel cells. Additionally, the development of catalysts for the utilization of fuels other than H<sub>2</sub> (e.g. hydrocarbons, CH<sub>3</sub>OH, CO) is needed. Improved attachment schemes for the catalyst should be pursued. The amount of Pt used must be lowered while retaining, or improving, the activity. Charge transport through electrode coatings requires additional study. Optimization of electrode textures is needed. Research of systems having fast start-up times, including room temperature, is needed.

#### General Batteries

Quite a range of research opportunities for batteries emerged from the discussions at the workshop. High priority was placed on diagnostic procedures: non-destructive evaluation, lifetime prediction, state of charge determination. Electrocatalysis in non-aqueous media, especially relating to high rate Li batteries was highlighted as a research opportunity. New thermal batteries (high energy density and low initiation and operation temperature) represents an area where little research effort is being expended and where the military represents the major applications. Solid state batteries are not being studied in the U. S., but could prove useful in low rate, long life applications. Aside from electrocatalysis in the Li batteries,

surface chemistry of the Li and chemistry of S compounds were identified as fruitful basic research areas. Development of Li/air and Li/Cl<sub>2</sub> batteries appears to represent an opportunity for new high energy battery systems. An ambient rechargeable Li battery would be a valuable development.

#### CONCLUSIONS AND RECOMMENDATIONS

Electrochemical energy sources are crucial to many military systems. New military developments require unique electrochemical devices where the needed research effort would yield negligible commercial payoff. Consequently, DOD must assume major responsibility for research and development of electrochemical energy sources to meet military needs. The particular programmatic responsibility of an agency of the DOD should be governed by the missions of the agency.

There is definitely a role for the DARPA/DSO in the area of electrochemical energy sources. Inasmuch as all of the generic problems involve materials issues, the DSO at least has the responsibility to maintain an awareness of the state of the technology. Second, DARPA should bear responsibility for the research necessary to undergird its own missions involving systems where new electrochemical energy sources are needed. And finally, the DARPA/DSO should support innovative, high-risk proposals that could lead to the development of new electrochemical energy sources needed by the military.

The innovative, high risk proposals could involve approaches to solving major problems such as the O<sub>2</sub> reduction

kinetics that would have broad impact on fuel cells and metal/air batteries. Another area would be electrode oxidation catalysts for  $\text{CH}_3\text{OH}$  or hydrocarbons to allow the direct use of liquid fuels in a fuel cell. In another direction, the use of  $\text{F}_2$  as an oxidant might be possible if new materials for storing  $\text{F}_2$  could be synthesized. Novel approaches to new high rate, high energy density electrochemical energy sources should be supported. The  $\text{Li}/\text{BrF}_3$  system is the sort of approach that could, in principle, be workable and merits further consideration.

#### ACKNOWLEDGEMENT

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#### REFERENCE

"Assessment of Research Needed for Advanced Battery Systems," Publication NMAB-390, National Academy Press, Washington, D. C., 1982.

MATERIALS RESEARCH COUNCIL  
WORKSHOP ON ELECTROCHEMICAL ENERGY SOURCES

July 11-12, 1983

July 11

Introduction and Welcome, M. S. Wrighton, MRC and MIT

DARPA Interests, R. A. Reynolds, DARPA

Navy Research and Interests, J. Smith, ONR

Air Force Research and Interests, W. S. Bishop, WPAFB

"Overview of Practical Battery Systems, R. J. Brodd,  
Consultant to DOE

"Electrochemical Vehicle Propulsion Systems", E. Cairns,  
UC, Berkeley

"Primary Lithium Batteries". D. Linden, Consultant to  
Mallory

"Fuel Cells and Their Limitations", F. C. Anson, Cal.  
Tech.

"Metal Air Batteries-An Overview", F. G. Will, GE R&D

Summary Discussion of the State of Practical Electro-  
chemical Storage and Conversion

July 12

"Polyacetylene: A Materials for Batteries",  
A. G. MacDiarmid, Univ. of Penn.

"Polymer-Based Battery Research at Allied",  
L. Shacklette, Allied Chemical

"Recent Studies of Polyacetylene at GE", F. G. Will,  
GE R&D

Promises and Problems for Polymer-Based Batteries

Opportunities for DARPA:

- (1) Fuel Cells, F. Anson, E. Cairns;
- (2) Polymers, A. MacDiarmid, L. Shacklette;
- (3) Emerging Opportunities, F. Will, R. Brodd, and  
M. Wrighton.

[The thrust of this session is to identify materials  
problems, new systems, research areas, limitations, etc.  
that should be brought to DARPA's attention.]

MATERIALS RESEARCH COUNCIL  
WORKSHOP ON ELECTROCHEMICAL ENERGY SOURCES

July 11-12, 1983

Attendance List

<u>Name</u>	<u>Affiliation</u>	<u>Business Phone</u>
M. Wrighton	M.I.T./MRC	(617)253-1597
H. Ehrenreich	Harvard/MRC	(617)495-3213
G. Ramsay	Gould, Inc.	(312)640-4581
A. MacDiarmid	Univ. Of PA.	(215)898-8307
L. Shacklette	Allied Corp.	(201)455-4991
E. Cairns	UC Berkeley	(415)486-5028
F. Anson	Caltech	(213)356-6000
D. Reynolds	DARPA	(202)694-1959
J. Smith	ONR	(202)696-4410
F. Will	General Elec.	(518)385-8635
R. Brodd	DOE/Consultant	(202)252-1486
G. Caprioglio	GA Technologies	(619)455-4156
D. Linden	Duracell	(914)591-7000
W. Clark	GTE Laboratory	(617)466-2171
T. McGill	Caltech/MRC	(213)356-4849
J. Margrave	Rice/MRC	(713)527-4813
K. Bowen	M.I.T./MRC	(617)253-6892
A. Garito	U. of Penn.	(215)898-5810
S. Roosild	DARPA	(202)694-5800
B. Carnahan	Univ. Michigan	(313)764-3366
W. Bishop	USAF/AFWAL	(513)255-6235

## HIGH ENERGY SURFACE REACTIONS

J. L. Margrave

On July 12-13, 1983, presentations oriented to the elucidation of high-energy surface reactions at a fundamental level were given as outlined in the program. Attendances ranged from 16-20. These areas were also reviewed at the DARPA/BDM laser countermeasure program, held on July 18-22 at the S-Cubed facility. A more general, in-depth discussion of laser hardening concepts and their practical achievements occurred there.

Presentations on July 12 were concerned with the physics/chemistry of radiation-solid interactions at wavelengths ranging from the far UV to the IR ( $10.6\ \mu$ ) at energy intensities over the range 1-1000 Kw/cm<sup>2</sup>. Dr. Tom Schriempf of the Naval Research Laboratory discussed typical experiments which compare methods for protecting Al from laser irradiation, especially at the  $<10\ \text{Kw/cm}^2$  level. Paints, resins, and spray-on refractory coatings are all used and provide some protection in this low-energy regime. Actually, metal reflectivity is sufficiently high that it provides considerable protection, but in real-world situations Al-surfaces weather and become good absorbers. An interesting solution to this problem is the cleanly ablating resin which gives good protection from weathering (salt water, industrial smoke/dust, etc.) and yet ablates off under irradiation to leave a clean, high-reflectivity Al-surface.

Dr. David Golden of SRI International discussed applications of lasers in high-temperature gas kinetic studies and in



studies aimed at identifying first steps in the initiation of the explosion of unstable solids like TNT. Studies of the laser-induced decomposition of mono-, di- and tri-nitro-aromatic compounds are in progress at SRI. Bond-specific steps in decomposition mechanisms can be identified by this approach. One advantage of a laser-heated gas system is the opportunity to minimize wall effects, since a homogeneous high-temperature environment is provided. By using different "heater" gases and different laser wave-lengths, it is possible to work in a variety of chemical environments. For example,  $\text{SF}_6$  is an excellent infrared absorber (heater gas) at  $10.6 \mu$ .

The Center for Laser Studies at the University of Southern California is directed by Dr. Michael Bass. He described the laser systems available at the Center and several of their projects. Research areas ranged from laser development and development of wave-guides and high-transmission fibers for directing laser energy to a wide-range of fundamental/applied studies conducted through collaborative projects involving the center staff and faculty/students from various university departments--materials science, physics, chemistry, etc.

Dr. S. Copley from USC discussed studies of laser CVD processes and progress in developing techniques for using  $\text{CO}_2$ -lasers (300-900 W) for precision machining of  $\text{SiC}$  and  $\text{Si}_3\text{N}_4$ . Special techniques using polarized beams were described.

The fundamentals of electron beam and ion beam heating processes were discussed by Dr. Frank C. Perry of the Sandia

Laboratories in Albuquerque. Although differing in the details of how the energy is absorbed, the effects of similar energy depositions from electron beams and laser beams in the 1-100 kW/cm<sup>2</sup> range appear to be directly comparable. Thermal and dynamic responses of Al and Cu to electron beam heating pulses have been quantitatively measured.

A discussion of laser-solid and electron beam-solid interactions was led by Dr. Michael J. Berry from Rice. Thermal heating effects were contrasted with photochemical effects for various wave lengths. Also, CW vs. pulsed heating exposures may yield different species and different performance ratings.

The DARPA/BDM program was discussed on the second day of the meeting. Dr. C. M. Stickley of BDM presented an overview of the Raytheon studies done in the March-May, 1983, period at the UTRC DF-laser Facility. A highly sophisticated diagnostic system for simultaneous, real-time monitoring of many parameters was assembled. Among the measured quantities and observations were:

- (a) Laser power and beam profile
- (b) Sample reflectance
- (c) Front surface thermal image (IR)
- (d) Front surface temperature
- (e) Back surface temperature
- (f) Burn-through time
- (g) IR emission from vaporized gases
- (h) VIS/UV emission from vaporized gases

- (i) Weight loss of ablated sample
- (j) Edge temperature of heated sample
- (k) Crater profile
- (l) Video recording of each laser shot
- (m) etc.

Of 196 total laser shots, some 135 were actual irradiations of 13 different materials and 115 of these were well-documented by the diagnostic tools available. Data from the runs were stored in the computer management system and are currently under analysis. Detailed comparisons of experimental results and predictions based on theoretical models agree well for the systems analyzed thus far.

The current figure-of-merit for materials tested in the UTRC configuration (1.5 cm dia x 3 mm thick cylindrical disks) is the time to burn through the sample at 18 kW/cm<sup>2</sup> peak power. Experimental data show burn-through times ranging from 0.9 sec to over 4 sec, with the best performances by TBR-type materials and pyrographite. Not surprisingly, phenolic-based charring ablators had the shortest burn-through times.

A micro-scale version of these tests is being conducted in parallel at Rice University with a ~100 watt HF/DF laser system producing energy densities over the 10-1000 kW/cm<sup>2</sup> range on small samples (~1-3 mm dia x 1 mm thick, cylindrical disks). Simultaneous real-time measurements of laser power, laser profile, laser jitter, front-surface temperature (two-color pyrometer), burn-through time and reflectance have been made.

Weight-loss, crater shapes, and other post-irradiation studies of samples are also available. Again, burn-through time appears to be a most useful figure-of-merit, and available results correlate qualitatively with the UTRC-large disk data.

Also reported from Rice were new measurements which characterize the (gaseous) species being evaporated or sublimed at the high temperatures. Mass-spectrometric studies of graphnol and TBR-based materials showed mainly  $C_3$  (gas) as the vapor species and this was confirmed by matrix-isolation IR studies of the condensed vapor in argon at  $\sim 1:100,000$  dilution.

Completing the experimental report of the DARPA/BDM program activities was a presentation by Dr. Michael Frish outlining the electron-beam heating studies at PSI in Andover, Massachusetts. This device allows heating of cylindrical disk samples which are 0.5 cm in diameter and 1-5 mm thick at energy intensities up to  $\sim 9 \text{ kW/cm}^2$ . The electrons are accelerated across an 8 keV potential difference and deposit their energy in the first few microns of the target. Electron beam studies require a fairly high vacuum ( $\sim 10^{-5}$  torr) and also a conductive sample.

Several important experimental results have come from the electron-beam studies. Measurements of monochromatic emissivities (Reflectance =  $1 - \text{Emissivity}$ ) at various wave-lengths ( $2.7 \mu$ ,  $10.6 \mu$ , etc.) were reported for hot samples as a function of time. Roughening of heated graphnol samples led to emissivity changes, usually to increased emissivity, and thus to decreased reflectance. In contrast, heating of TBR samples led to a

"metalling" of the surface, probably due to the formation of molten metal carbides, and to a reduced emissivity, i.e., higher reflectance. Also, weight losses of cratered samples were measured.

The emissivity measurements and weight losses reported by PSI and thermophysical properties for graphite-based materials from the literature have been used for modelling/scaling calculations at PSI, Raytheon and BDM. Calculated crater contours and burn-through times agree well with the UTRC-experiments for the samples which have been considered. Similar modelling correlations for the micro-scale experiments are being developed.

After these presentations, a discussion of the materials development programs underway at Acurex in Palo Alto, at General Electric in Philadelphia and at McDonnell-Douglas in Los Angeles occurred. Various laser hardening concepts, ranging from paints and spray-on coatings to carbon-carbon composites, ablating phenolics and metal-loaded systems like TBR's, were considered. The possibilities of anomalous vaporization kinetics, e.g., metal carbides might yield mainly  $C_1$  as vapor species, as well as the outstanding performance of pyrolytic graphite were discussed.

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